

**Isodisperse Telechelic Polymers and their Polyurethane Derivatives  
Sample Preparation**

**Final Technical Report**

by

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## Abstract

This report describes the preparation of six hydroxy-terminated polybutadiene (HTPBD) samples and their hydrogenated (polyethylene) derivatives (HTPE). The polybutadiene samples, with nominal average molecular weights  $M_n$  of 1000, 1500, 2000, 3000, 5000, and 10000, have been prepared using the so-called "isodisperse telechelic polymerization" method under non-isothermal conditions. The HTPBD samples produced were characterized by gel permeation chromatography, FT-IR and  $^1\text{H}$ -NMR and showed a narrow polydispersity approaching the theoretical limit. From the HTPBD samples isodisperse HTPE samples were prepared by hydrogenation under heterogeneous conditions, using a freshly prepared 30% palladium/charcoal catalyst. Between July 1995 and May 1997, 100-g batches of the twelve samples thus prepared were sent to the US army research laboratory for further experiments.

**Keywords:** isodisperse telechelic polymerization, hydroxy-terminated polybutadienes, hydroxy-terminated polyethylenes, non-isothermal polymerization, hydrogenation

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## Introduction

In the past decade there has been a great interest in hydroxy telechelic polymers with designed low molecular weights and narrow polydispersity. There may be several applications for this type of polymers:

- ◆ Incorporation into a polymeric matrix to alter its physical properties such as viscosity.
- ◆ Chemical modification of the reactive sites: the hydroxy end groups can be converted into acrylic, acid or acid chloride groups.
- ◆ Crosslinking with multifunctional reagents to obtain macromolecular networks.

Free-radical polymerization is probably the most cost-effective for preparing such polymers with functional groups in the  $\alpha,\omega$  positions [2, 3]. In that case the functionality is determined by the nature of the initiating radicals. However, controlling polydispersity has often been a problem in free-radical polymerizations. This is mainly related to changing conditions during the polymerization reaction: decreasing concentrations of initiator and monomer, and increasing viscosity. At the Research Group of Macromolecular Chemistry of the Hungarian Academy of Sciences, a method was developed to counteract these effects and produce polymers with minimal polydispersity  $P_w/P_n$  [4]. In theory, in the case of recombination, the polydispersity P.D. equals 1.5 and the functionality  $F$  of the polymer equals 2.

The US Army Research Laboratory is interested in obtaining elastomers with optimal physico-chemical properties. Isodisperse telechelic polymers such as HTPBD or HTPE could constitute such materials according to the theory of elasticity. This report describes the synthesis and chromatographic/spectroscopic characterization of six HTPBD samples with nominal average molecular weights  $M_n$  of 1000, 1500, 2000, 3000, 5000, and 10000. The optimization of the reaction conditions and the development of the corresponding temperature programs has been described in detail in our previous report "Isodisperse Telechelic Polymers and their Polyurethane Derivatives" (contract # N68171-95-C-9068) [1]. Six HTPE samples were then prepared from their HTPBD precursors through hydrogenation using a palladium/charcoal catalyst. The twelve samples were sent to the US Army Research Laboratory in 100-g amounts for further characterization.

## Experimental

### Chemicals

4,4'-azo bis-4-cyano-*n*-pentanol (ACP) synthesized in our own laboratory from 5-hydroxy-2-pentanone (Fluka); molecular weight: 252; melting point: 81-83 °C or 94-96°C (two isomers). Hydrogen peroxide, 50% solution by weight, from Peroxid Chemie GmbH, Germany. 1,3-butadiene, purity > 99% from Matheson.

### Polymerization

The polymerization reactions were carried out in an acid-proof autoclave from Parr (net volume 900 ml; maximum pressure 190 bar). The reactor can be stirred mechanically, electrical heating and cooling with circulating water can be applied from the outside. After addition of all solvents and dissolution of the initiator the reactor is flushed with pure nitrogen and evacuated several times. Then the monomer (preheated to 30°C) is added in liquid form from a buffer vessel and the polymerization reaction is started according to a specific temperature program.

### Purification

After the polymerization reaction the pressure is released and the unreacted monomer is condensed and recovered. The recombination product from initiator and hydrogen peroxide is removed by washing with distilled water in a separation funnel. The remaining peroxide is reduced to below 1 ppm level by passing through a zeolite column activated with cobalt ion. The solvents are removed in a film evaporator by nitrogen heated to 140°C [1].

### Hydrogenation

3 g of freshly prepared 30% Pd/C catalyst and 30 ml of *n*-hexane was placed in a Parr hydrogenation apparatus. After repeated flushing/evacuation with nitrogen and then with hydrogen the catalyst was hydrogenated for 20 minutes at 60°C and 4 bar. Then 10 g of the HTPBD sample was added in 370 ml of *n*-hexane and was hydrogenated at 60°C and 4 bar during 1 hour. After filtration over a glass filter the catalyst was washed and the solvent was evaporated under vacuum. Eleven batches were prepared and combined to yield the amount required. Heating to 100°C under reduced pressure served to remove the last traces of solvent. See also ref. [5].

### Instrumental Analysis

Proton NMR spectra were recorded using a Varian 400 instrument. Fourier transform infrared spectra (FT-IR) were recorded using a Bomem MB-100 spectrophotometer. The molecular weight distribution was determined by means of gel permeation chromatography (GPC) using a setup from Waters: pump model 510, injector model U6K and a set of four columns packed with crosslinked polystyrene gel ("ultrastaygel") of particle size less than 10 microns and pore sizes of 10 µm, 1 µm, 100 nm and 50 nm.

The functionality of the polymers was calculated from the hydroxy-endgroup concentration and the molecular weight of the polymers, as described in our previous report [1]. The apolar solvent used (cyclohexane) precludes any interference from the ACP initiator recombination product, as it is insoluble in this solvent.

## Preparation of HTPBD Samples

Polybutadiene samples were synthesized with nominal average molecular weights  $M_n$  of 1000, 1500, 2000, 3000, 5000, and 10000. The polymerization conditions applied are listed in Table 1. The details of the non-isothermal temperature programs have been described earlier [1].

Table 1: Polymerization conditions and reagents used.

Samples	Monomer	Solvent (ml)		Initiator (mol/l)		Polym. time (min)	Temp. °C
	mol/l	sec. butanol	dioxane	ACP	H <sub>2</sub> O <sub>2</sub>		
HTPBD-1000	6.0	200	200	0.145	-	175	73-96
HTPBD-1500	6.0	200	200	0.145	-	500	65-96
HTPBD-2000	6.0	400	-	2.14E-02	0.63	180	80-96
HTPBD-3000	6.0	400	-	2.14E-02	0.53	360	75-96
HTPBD-5000	6.0	400	-	5.73E-03	0.18	480	70-96
HTPBD-10000	6.0	200	200	8.00E-04	6.15E-03	720	70-96

The functionality of the HTPBD samples was determined and was found to be close to the theoretical value of 2 for all samples (see Table 2). The conversion rates of the polymerization reactions varied between 20 and 40% for most samples, but was only 10% for the HTPBD-10000 sample (see Table 2). The experimentally determined average molecular weights and polydispersity data (as measured by GPC) are also listed in Table 2 and visualized in Figure 1.

Table 2: Functionality, conversion rates and polydispersity of HTPBD samples

Samples	Functionality	Conversion	GPC results	
		%	$M_n$	$M_w/M_n$
HTPBD-1000	1.62	30.0	1245	1.34
HTPBD-1500	2.10	33.0	1552	1.34
HTPBD-2000	1.90	20.0	1870	1.62
HTPBD-3000	2.44	40.0	3250	1.98
HTPBD-5000	1.98	25.0	5230	1.72
HTPBD-10000	1.97	10.0	10800	1.95

As shown in Table 2, the molecular weight distribution of the samples HTPBD-1000 and HTPBD-1500 is very low, even below the theoretical value of 1.5. These low polydispersities can be expected to have a very positive effect on the elastic properties of the resulting polyurethane materials according to the elasticity theory.

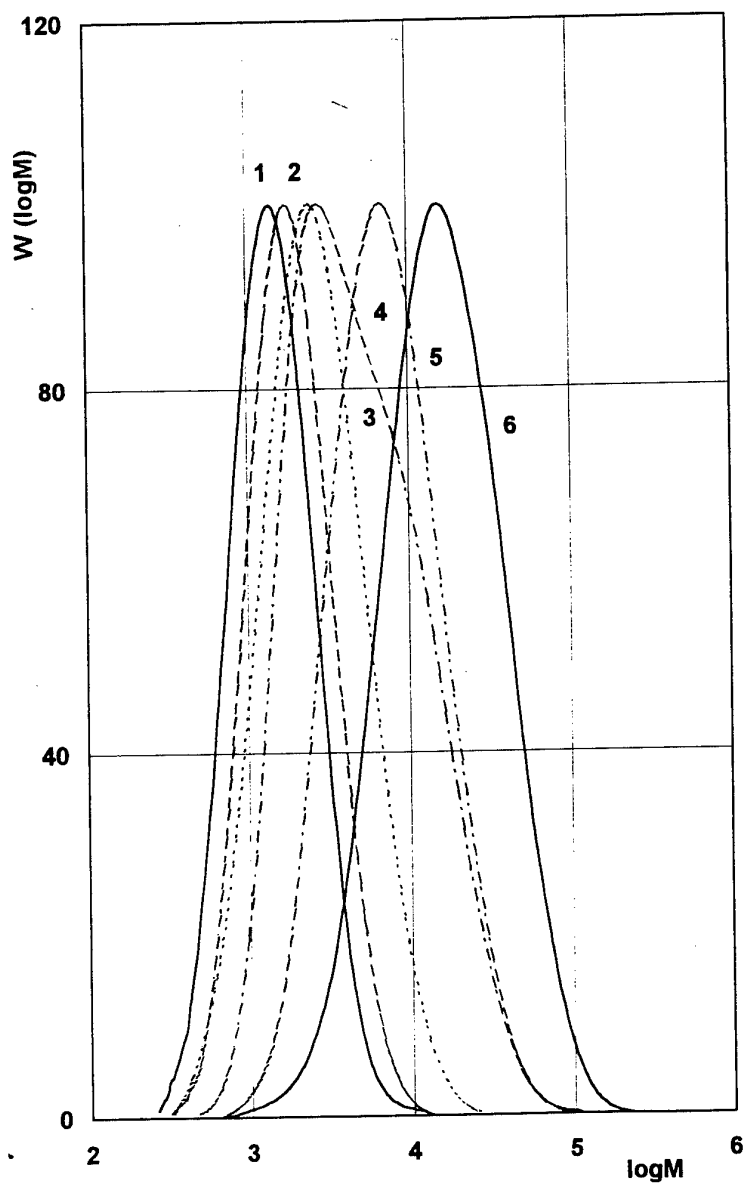


Figure 1: Molecular weight distribution of the HTPBD samples, as determined by GPC. 1= HTPBD-1000; 2= HTPBD-1500; 3= HTPBD-2000; 4= HTPBD-3000; 5= HTPBD-5000; 6= HTPBD-10000.

The microstructure of the HTPBD samples was investigated using FT-IR and  $^1\text{H}$ -NMR spectroscopy; the spectra can be found in Annex 1. The FT-IR spectra show only a few differences between the samples. Obviously the broad OH-stretch absorption at 3200-3600  $\text{cm}^{-1}$  (hydroxy endgroups) is relatively strong for the short oligomers and practically invisible for the HTPBD-5000 and HTPBD-10000 samples. For the same reason the cyanide stretch vibration (initiator fragments) is most strongly observed in the spectra of the shortest oligomers.

During the course of the polymerization three different configurations can be formed: 1,4-trans, 1,2- and 1,4-cis linkages. The distribution of these linkages was determined based on the ratios of a number of out-of-plane IR vibrational absorptions, as described in our previous report [1]. The ratio between the number of 1,2-linkages and 1,4-linkages was also determined by proton NMR spectroscopy; the two configurations can be distinguished based on the unsaturated proton intensities at 4.9-5.0 and 5.2-5.4 ppm, respectively [1]. In general, the results of the two techniques agree quite well, although in general the percentage of 1,2-linkages appears to be a little higher according to the NMR results in comparison to the FT-IR results (see Table 3). In general, the ratio of 1,2-linkages vs. 1,4-linkages is about 1 to 5 in all samples, irrespective of the average chain length.

Table 3: Microstructure of HTPBD samples based on FT-IR and NMR results (%).

Samples	FT-IR			proton NMR	
	1,2 link	1,4 link <i>cis</i>	1,4 link <i>trans</i>	1,2 link	1,4 link
HTPBD-1000	11	54	35	15	85
HTPBD-1500	11	58	31	15	85
HTPBD-2000	13	54	33	17	83
HTPBD-3000	13	53	34	18	82
HTPBD-5000	13	54	33	17	83
HTPBD-10000	13	59	28	14	86

## Preparation of HTPE Samples

Before the hydrogenation, new batches of HTPBD were prepared, using approximately the same conditions as those employed for the first set of HTPBD samples. The resulting products were analyzed by GPC, FT-IR and proton NMR, and the OH-functionality was also determined. Again the resulting polydispersities were quite narrow ( $1.5 < 2$ ) and again the polydispersity was smallest in the case of samples HTPBD-1000 and HTPBD-1500 (see Table 4). Using the same method as described above, FT-IR and proton NMR spectroscopy was employed to determine the distribution of 1,2-linked *vs.* 1,4-*trans* linked *vs.* 1,4-*cis* linked configurations of these precursor HTPBD polymers and the results were very similar to those obtained with the first batch (compare Table 3 and Table 5). Most of these structural investigations were carried out on the precursor HTPBD polymer rather than on the HTPE endproduct, as the solid nature of the polyethylene samples and their insolubility in most solvents would preclude such measurements of the endproduct, unless extremely powerful solvents such as trichlorobenzene and very high temperatures were used. Under the mild hydrogenation conditions applied in our laboratory the structural characteristics of the HTPBD chains (length, configuration of linkages) will remain unchanged and will therefore also describe the HTPE polymer samples. Of course the molecular weight of the oligomers will increase by 3.7 % due to the addition of two hydrogens per butadiene group.

*Table 4: Functionality and polydispersity of precursor HTPBD samples used for the preparation of hydroxy-terminated polyethylene.*

Samples	Functionality	GPC results	
		$M_n$	$M_w/M_n$
HTPBD-1000	1.98	1211	1.54
HTPBD-1500	2.03	1666	1.53
HTPBD-2000	2.01	2136	1.79
HTPBD-3000	2.05	3059	1.78
HTPBD-5000	1.97	5403	1.81
HTPBD-10000	1.99	10270	1.79

*Table 5: Microstructure of precursor HTPBD samples based on FT-IR and NMR (%)*

Samples	FT-IR			proton NMR	
	1,2 link	1,4 link <i>cis</i>	1,4 link <i>trans</i>	1,2 link	1,4 link
HTPBD-1000	11	54	35	17	83
HTPBD-1500	12	55	33	17	83
HTPBD-2000	11	55	34	17	83
HTPBD-3000	12	55	33	18	82
HTPBD-5000	12	54	34	17.5	82.5
HTPBD-10000	12	58	30	17.5	82.5

Hydrogenation of unsaturated polymers can, in principle, be accomplished in several ways. Several hydrogenation procedures were tested on small batches of polybutadiene polymer HTPBD-3000. Proton NMR was employed to determine the completeness of the reduction. Homogeneous catalysis with chloro-tris(triphenyl-phosphine)rhodium(I) was tested, and although the resulting product showed an almost complete reduction, the practical difficulties of removing catalyst traces from the product constituted a major drawback. Reductions under heterogeneous conditions with hydrazine hydrate as reducing agent and Raney-nickel or 10% Pd/C or PtO<sub>2</sub> as catalyst also failed. The best results were obtained using hydrogenated Pd/C in n-hexane. See the Experimental section and ref. [5] for further details on the hydrogenation experiments.

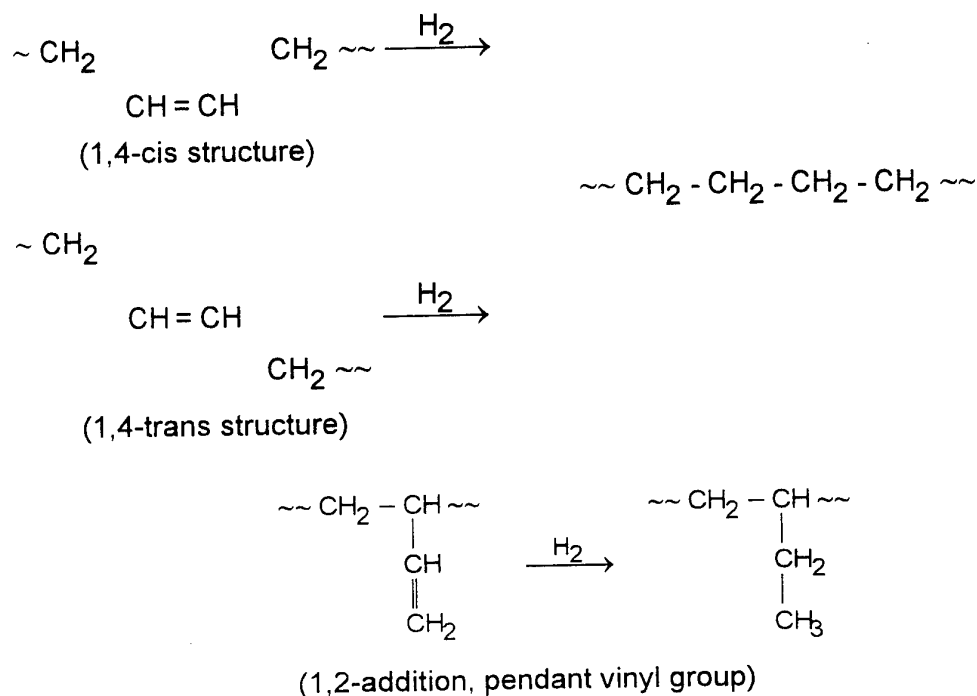


Fig. 2: Hydrogenation of 1,4-cis, 1,4-trans and 1,2 linked butadiene groups.

Figure 2 shows the structures resulting from hydrogenation of 1,4-linked and 1,2 linked polybutadienes. Given the mild hydrogenation conditions no structural changes or chain fission will occur. The hydrogenation of the above mentioned HTPBD samples led to the following products: HTPE-1000, HTPE-1500, HTPE-2000, HTPE-3000, HTPE-5000, HTPE-10000. These were analyzed by means of proton NMR before dispatching them to the US Army Research Laboratory (see Annex 2).

## Conclusions

In a previous stage of this project the optimal conditions for non-isothermal radical polymerization were theoretically derived and the corresponding temperature programs were developed. This report describes the successful application of this approach to the synthesis of bifunctional polybutadiene polymers with a uniform chain length. Indeed for all samples a narrow polydispersity  $M_w/M_n < 2$  was observed with gel permeation chromatography. The average molecular weights were usually well within 10-20 % of the target values.

From a second series of HTPBD samples showing similarly low polydispersity the corresponding saturated polyethylene derivatives were prepared by hydrogenation under heterogeneous catalytic conditions (Pd/C). One of the major advantages of this method is the easy separation and recovery of the catalyst.

This work has shown the potential of temperature-programmed radical polymerization for the production of polymers with uniform chain lengths. Application of these principles to the production of isodisperse copolymers has also been successful [6]. Such materials could ultimately be of great value for the production of cross-linked rubbers with excellent elastic properties.

*Table 6: HTPBD and HTPE samples shipped to the US Army Research Laboratory*

Samples	Shipping date	Mn
HTPBD-1000	Jan 25, 1996	1245
HTPBD-1500	Jan 25, 1996	1552
HTPBD-2000	Oct 13, 1995	1870
HTPBD-3000	July 6, 1995	3250
HTPBD-5000	Oct 13, 1995	5230
HTPBD-10000	Jan 25, 1996	10800
HTPE-1000	May 28, 1997	1256
HTPE-1500	May 28, 1997	1728
HTPE-2000	Feb 11, 1997	2215
HTPE-3000	March 7, 1997	3172
HTPE-5000	April 9, 1997	5603
HTPE-10000	April 9, 1997	10650

## References

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- 2 J.C. Brosse, M. Bonnier, and G. Legeay. *Macromol. Chem.* **183**, 313 (1982).
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- 4 Földes Pné, Gy. Mikétáné Fenyvesi, A. Nagy, T. Pernecker, Á. Rehák, D. Szalay, and F. Tüdös. Hungarian Pat: 201.101 (1986.11.14.) 4693/86; 1990.09.28; USA Pat. 5,126,415.
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- 6 F. Tüdös. Isodisperse Telechelic Polymers and their Polyurethane Derivatives. US Army contract # N68171-97-C-9002. 5th interim report (1998).

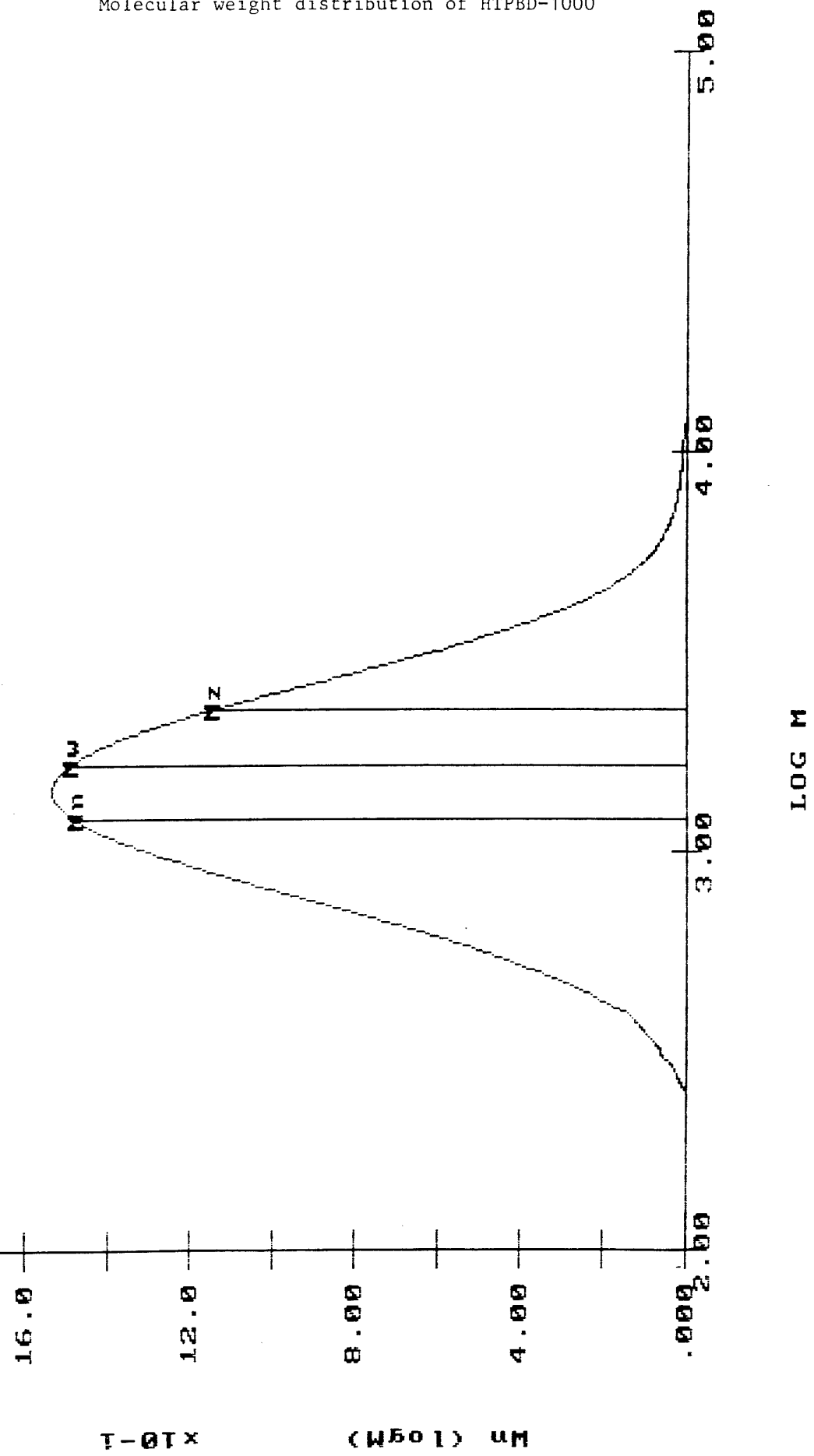
## **ANNEX 1**

### **CHARACTERIZATION OF HTPBD SAMPLES**

- ◆ Molecular weight distribution of HTPBD-1000
- ◆ Molecular weight distribution of HTPBD-1500
- ◆ Molecular weight distribution of HTPBD-2000
- ◆ Molecular weight distribution of HTPBD-3000
- ◆ Molecular weight distribution of HTPBD-5000
- ◆ Molecular weight distribution of HTPBD-10000
- ◆ FT-IR spectra of HTPBD-2000, HTPBD-3000, and HTPBD-5000
- ◆ FT-IR spectra of HTPBD-10000, HTPBD-1500, and HTPBD-1000
- ◆ Proton-NMR spectrum of HTPBD-1000
- ◆ Proton-NMR spectrum of HTPBD-1500
- ◆ Proton-NMR spectrum of HTPBD-2000
- ◆ Proton-NMR spectrum of HTPBD-3000
- ◆ Proton-NMR spectrum of HTPBD-5000
- ◆ Proton-NMR spectrum of HTPBD-10000

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 Mw = 1.67E3  
 Mz = 2.25E3  
 MOLECULAR WEIGHT DISTRIBUTION  
 HTPBD-1000

Molecular weight distribution of HTPBD-1000



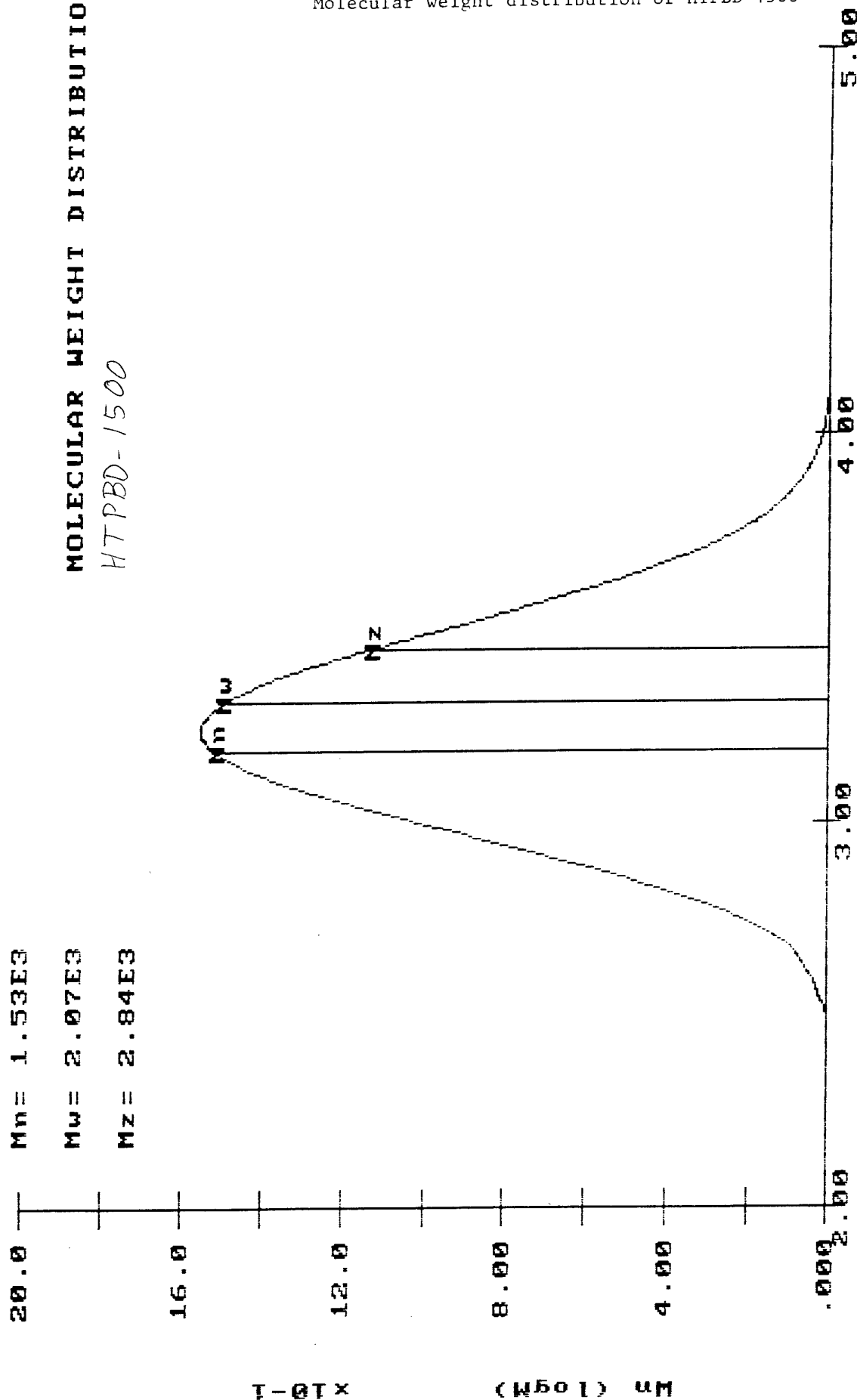
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MOLECULAR WEIGHT DISTRIBUTION

HTPBD-1500

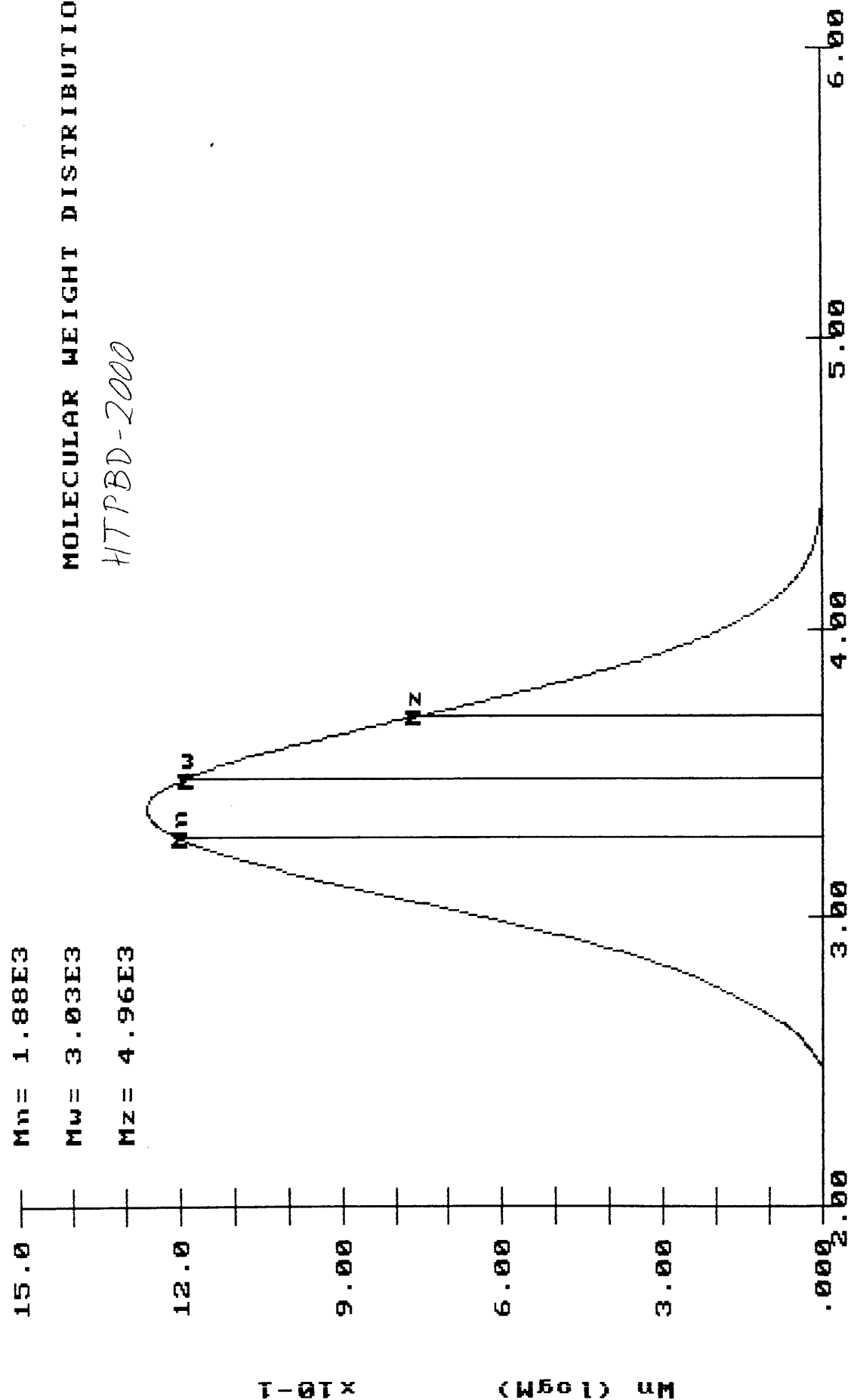
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Mw = 2.07E3  
Mz = 2.84E3

Molecular weight distribution of HTPBD-1500



LOG M

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 HTPBD-2000



100 M

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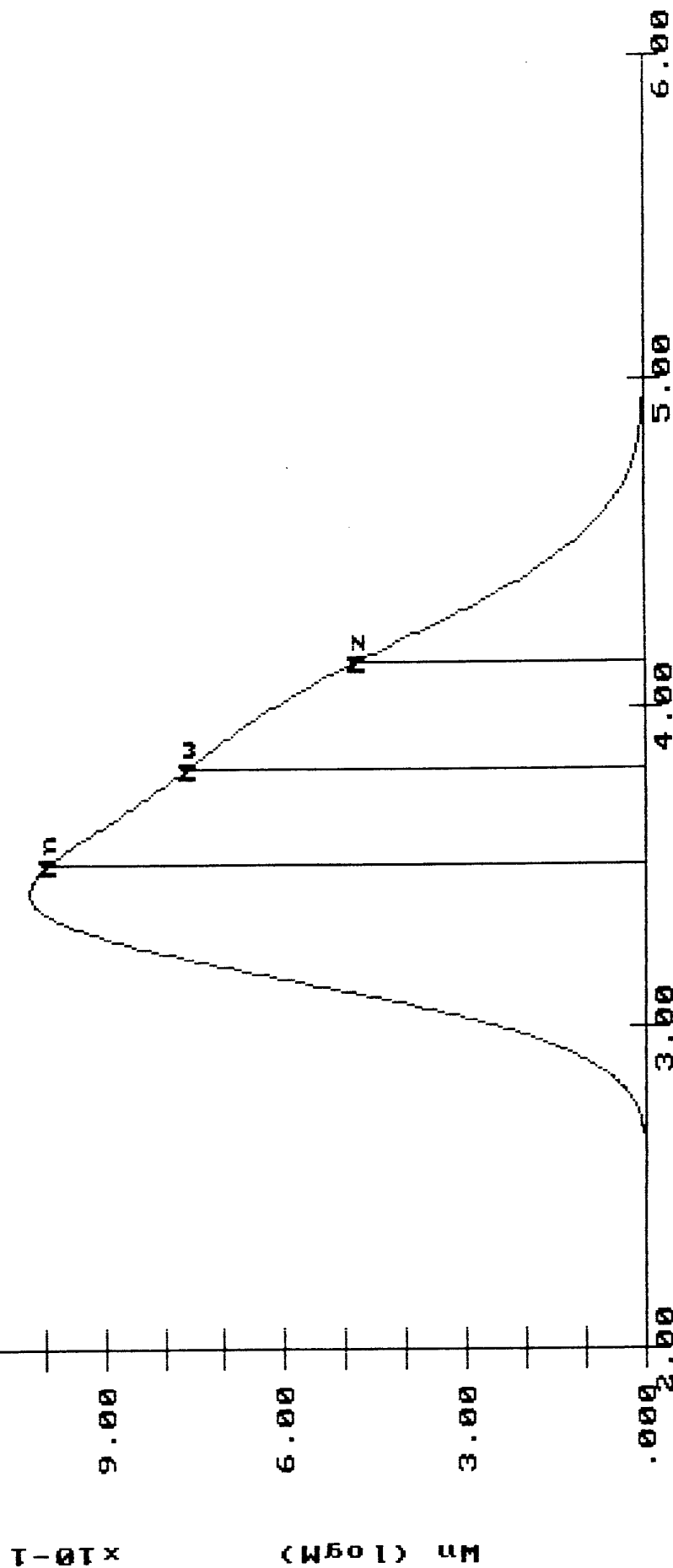
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HT PBD-3000



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Mw = 9.02E3

9.00

Mz = 1.57E4

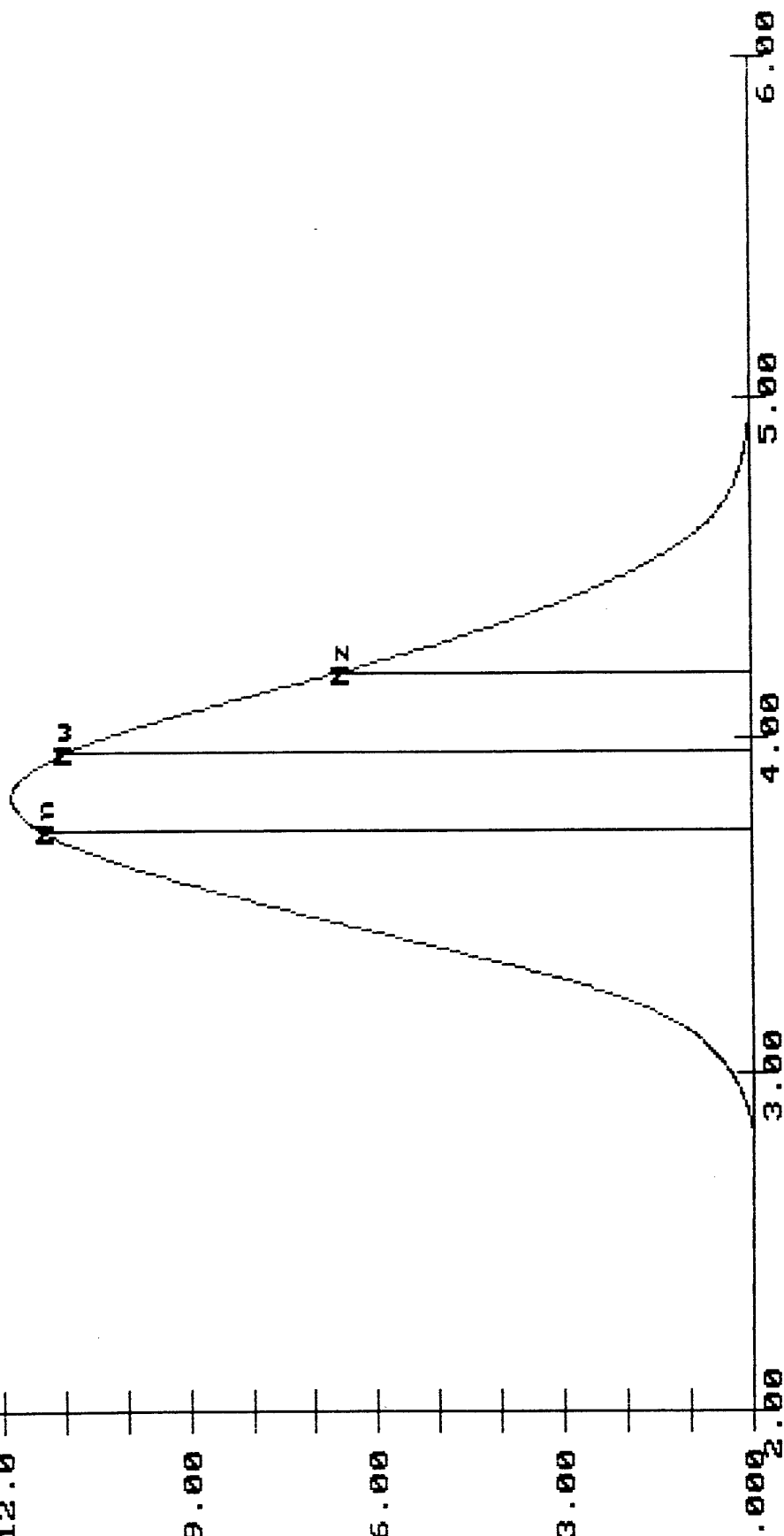
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1-01 x

(W501) 5E

MOLECULAR WEIGHT DISTRIBUTION

HT PBD-5000



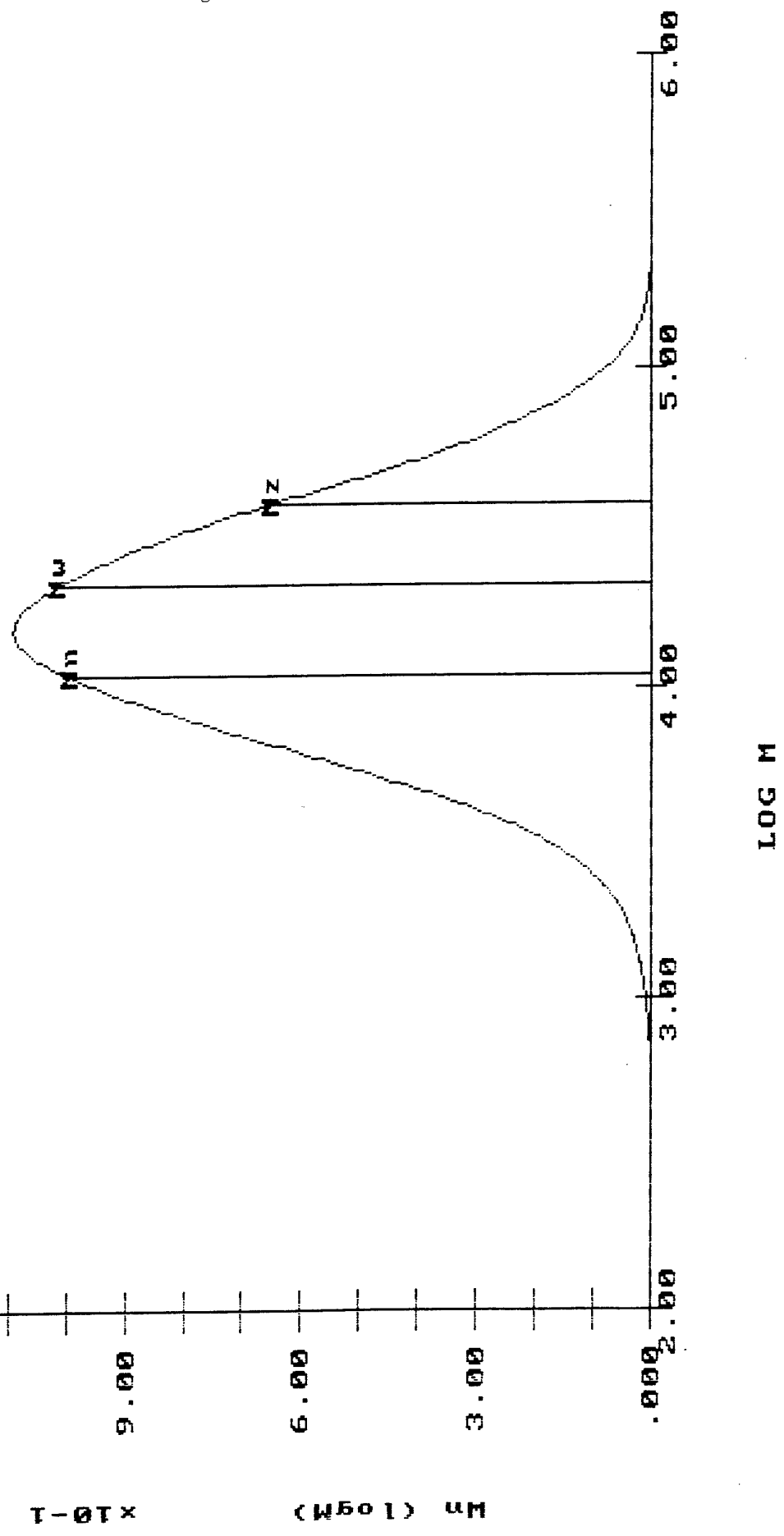
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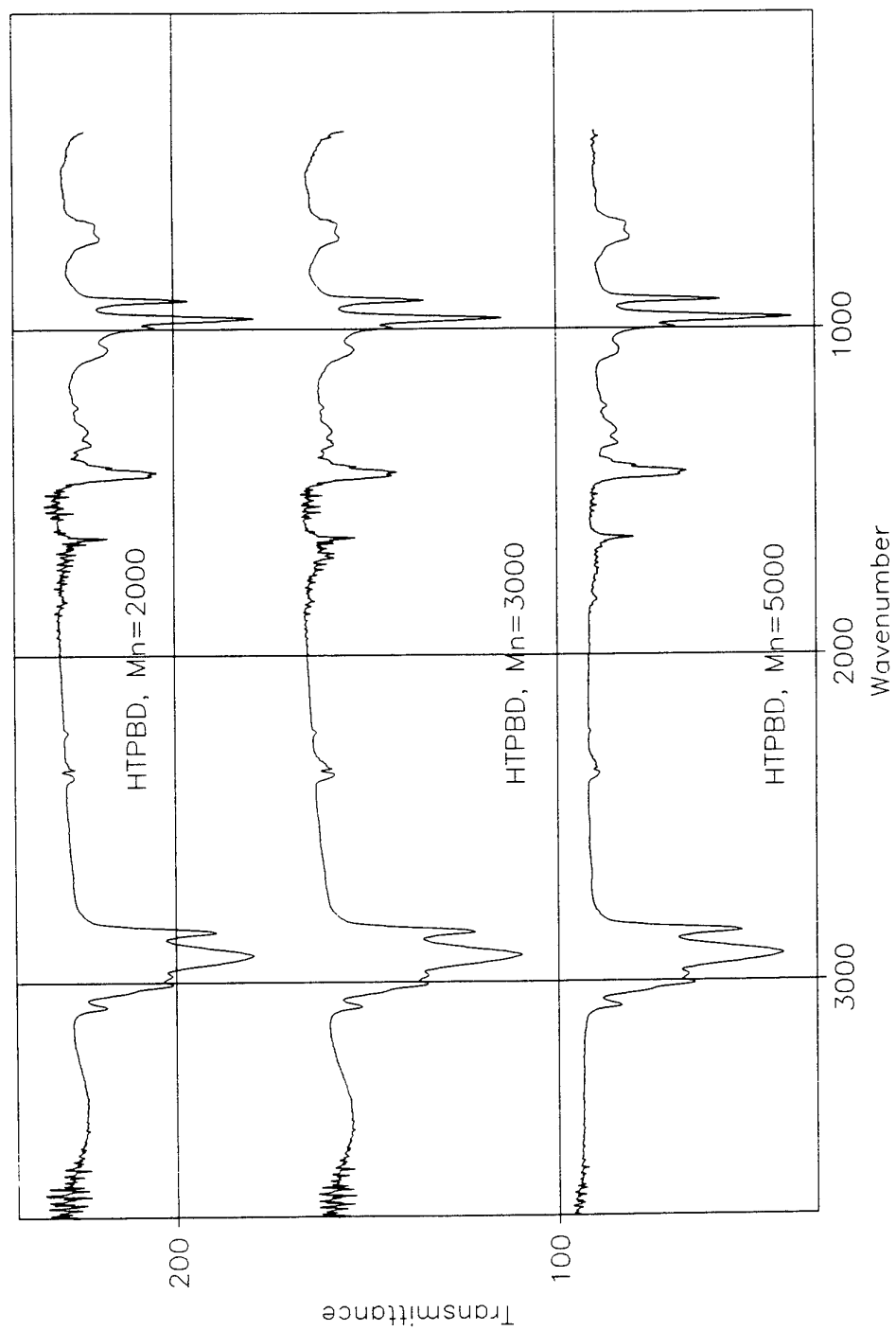
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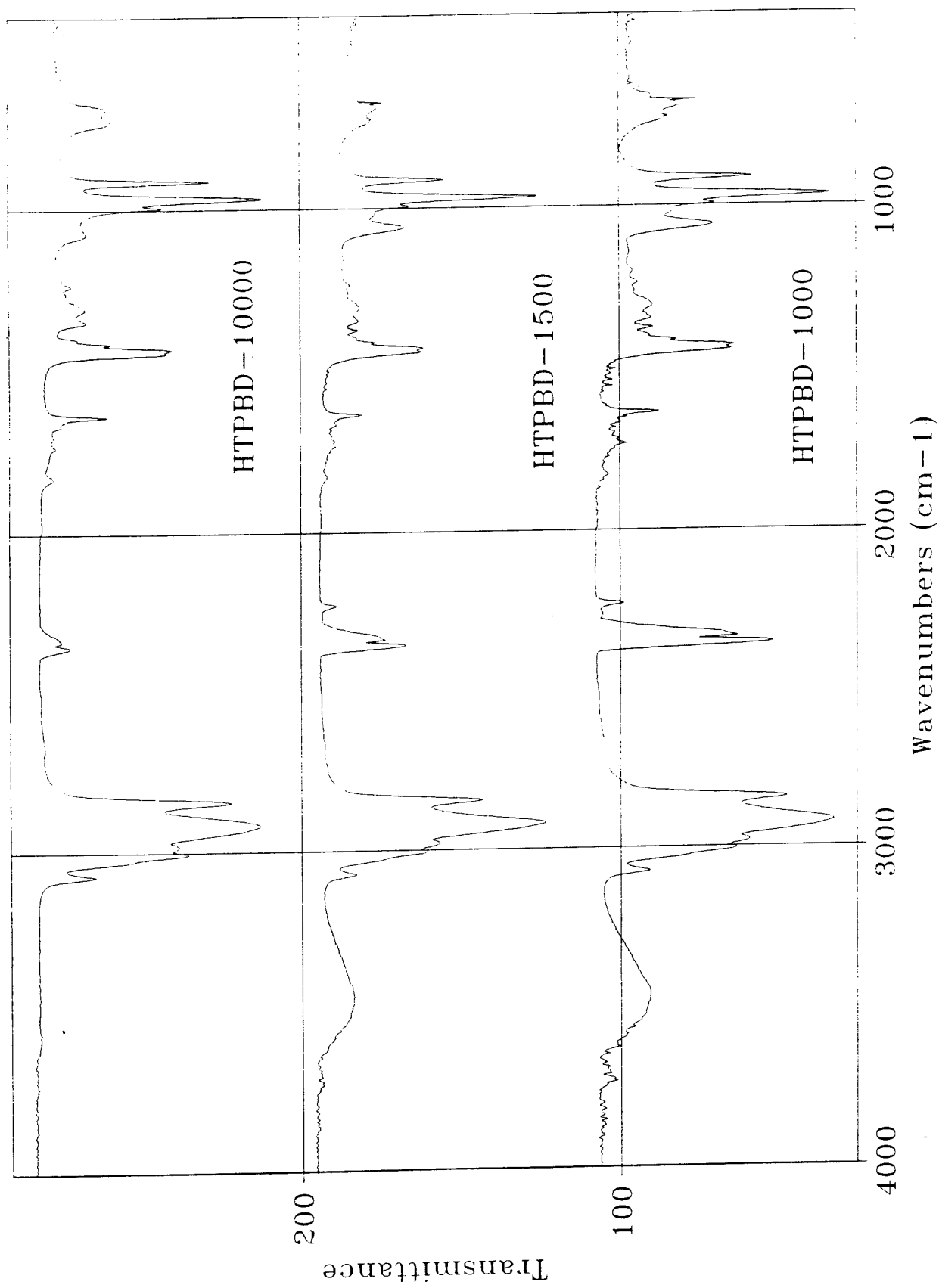
MOLECULAR WEIGHT DISTRIBUTION  
HTPBD-10 000

Molecular weight distribution of HTPBD-10000





FT-IR spectra of polybutadiene diol samples.



FT-IR Spectra of HTPBD samples.

<sup>1</sup>H-NMR spectrum of HTPBD-1000

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IS= 5v

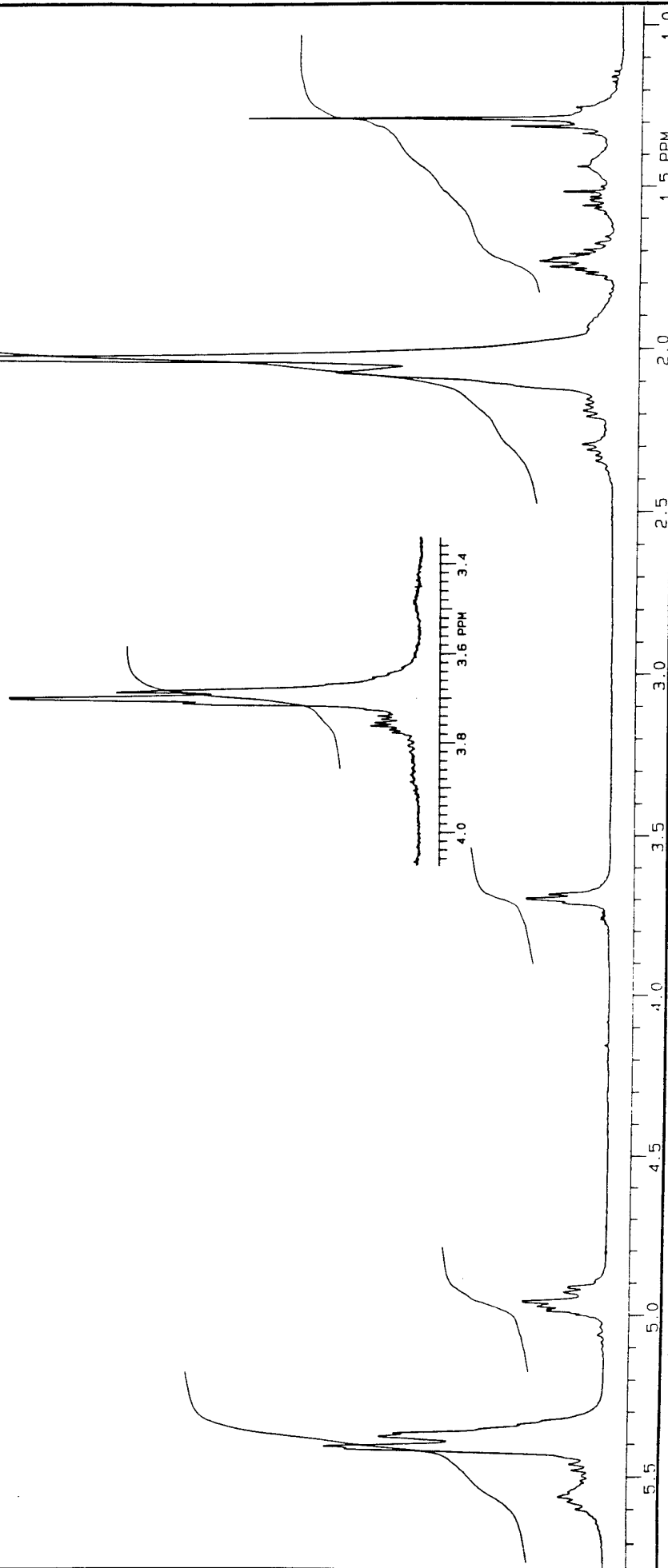
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5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 ppm

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Transmit	16	Power Mode	---	Start	372.1 Hz/ppm	---	---	---	05-01-96



400varian

$$\begin{array}{l} x \\ 5 = 51 \end{array}$$


3A0380

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 Acq. Time 3.994 sec      Delay 0 sec  
 Pulse Width 7.0 μsec      Transvers 16

374A03E

Nucleus 1.750      Offset 75.0 Hz  
 Mode NNN      Power 20 dB  
 Modulation Mode C      Freq 200 Hz  
 Pulse Width \_\_\_\_\_      Repeat Mode \_\_\_\_\_

**PL0T/PROCESSING**

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LB --- Hz AF --- sec COO ---  
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Reference ---

## EXPERIMENT

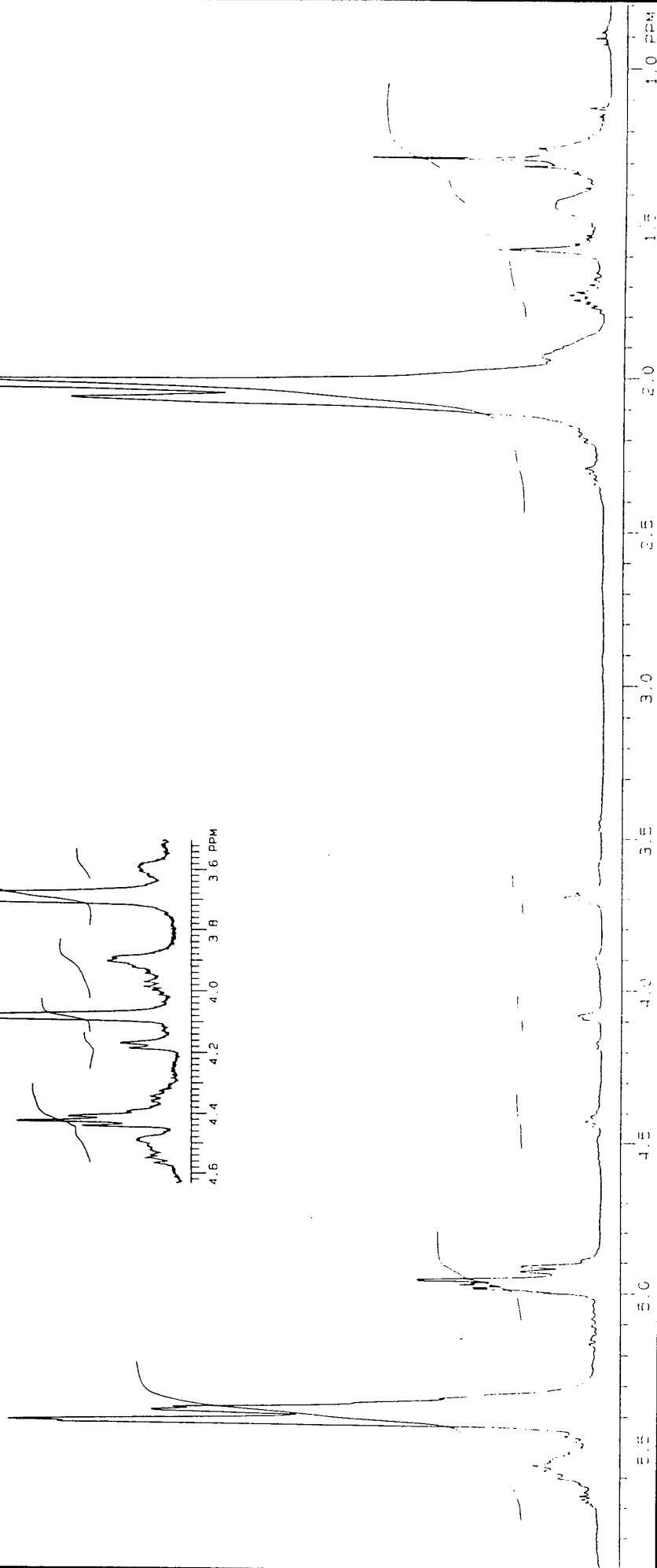
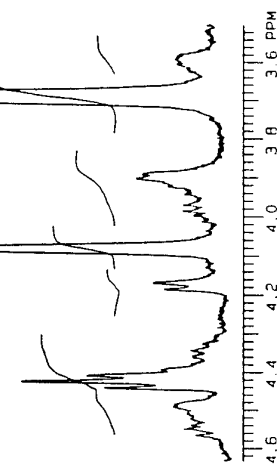
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 Temp            °C  
 Solvent            CDCL3

**SAMPLE**

SAMPLE  
H-8219 (19414)  
137 (CDCL3)  
KESZLER B./E.O.

Number \_\_\_\_\_  
 File \_\_\_\_\_ H \_\_\_\_\_  
 Date 05-01-96  
 xl VXR 400v

HTPBD-2000



Number HBE162  
 File 13-09-95  
 Date VXR 400 Varian

SAMPLE  
H-7378 (18600)  
POLIBUTADIEN (CCCL3) 78u-124  
KESZLER B.V.E. O.

Pulse Sequence STC14  
 Tube CD mm  
 Temp °C  
 Solvent CCCL3

EXPERIMENT

FN 32 32 32 32 32 32  
 LB --- --- --- --- --- ---  
 Width 2040.8 Hz nm nm nm nm  
 Reference ---

PLOT/PROCESSING

Offset 75.0 Hz  
 Power 20 db  
 Freq 200 Hz  
 Power Mode ---

Mode HNH  
 Modulation Mode C  
 Pulse Width --- μsec

DECOUPLE

Freq 400 MHz  
 Offset 327.0 Hz  
 Delay 0 sec  
 Transmits 16

Nucleus 13C  
 Spec Width 5000.0 Hz  
 Acc Time 3.374 sec  
 Pulse Width 7.0 μsec

OBSERVE

The figure displays a  $^1\text{H}$  NMR spectrum of HTPBD-3000. The x-axis represents the chemical shift in ppm, ranging from 1.0 to 6.0. The spectrum shows several distinct signals: a broad peak around 1.2 ppm, a sharp peak at approximately 1.5 ppm, a complex multiplet between 2.5 and 3.0 ppm, a sharp peak at 3.5 ppm, a broad peak at 4.0 ppm, and a sharp peak at 5.0 ppm. Four regions of the spectrum are expanded to show fine structure: 1) 4.2 to 4.1 ppm, showing a broad peak; 2) 3.9 to 3.6 ppm, showing a sharp peak; 3) 5.6 to 5.3 ppm, showing a complex multiplet; and 4) 5.0 to 4.90 ppm, showing a sharp peak with fine structure.

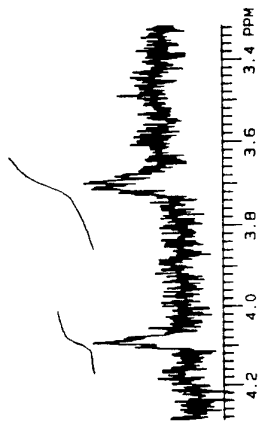
085874

The figure displays an NMR spectrum of 1,2-dichloroethane. The main spectrum shows a triplet at approximately 4.3 ppm and a quartet at approximately 1.8 ppm. An inset provides a detailed view of the triplet region, with a scale from 4.4 to 3.4 ppm. The inset shows the triplet structure more clearly, with a central peak and two side peaks. The main spectrum also includes a small peak at approximately 0.9 ppm, which is likely due to the solvent or a reference peak.

[illegible]

<sup>1</sup>H-NMR spectrum of HTPBD-10000

100.20  
100.20



Number \_\_\_\_\_  
 File \_\_\_\_\_  
 Date 05-01-96  
 XL VXR 400Varian

SAMPLE  
 H-8221 (19414)  
 HTPBD-10 (CDCL3)  
 KESZLER B / E. O.

Pulse Sequence \_\_\_\_\_  
 Tube ID \_\_\_\_\_  
 Temp \_\_\_\_\_ °C  
 Solvent \_\_\_\_\_ CDCL3

EXPERIMENT

IN \_\_\_\_\_ 32 K HE \_\_\_\_\_ sec CD \_\_\_\_\_ sec  
 LB \_\_\_\_\_ Hz AF \_\_\_\_\_ sec CD \_\_\_\_\_ sec  
 Width 1917.9 Hz/ppm Start 396.9 Hz/ppm  
 Reference \_\_\_\_\_

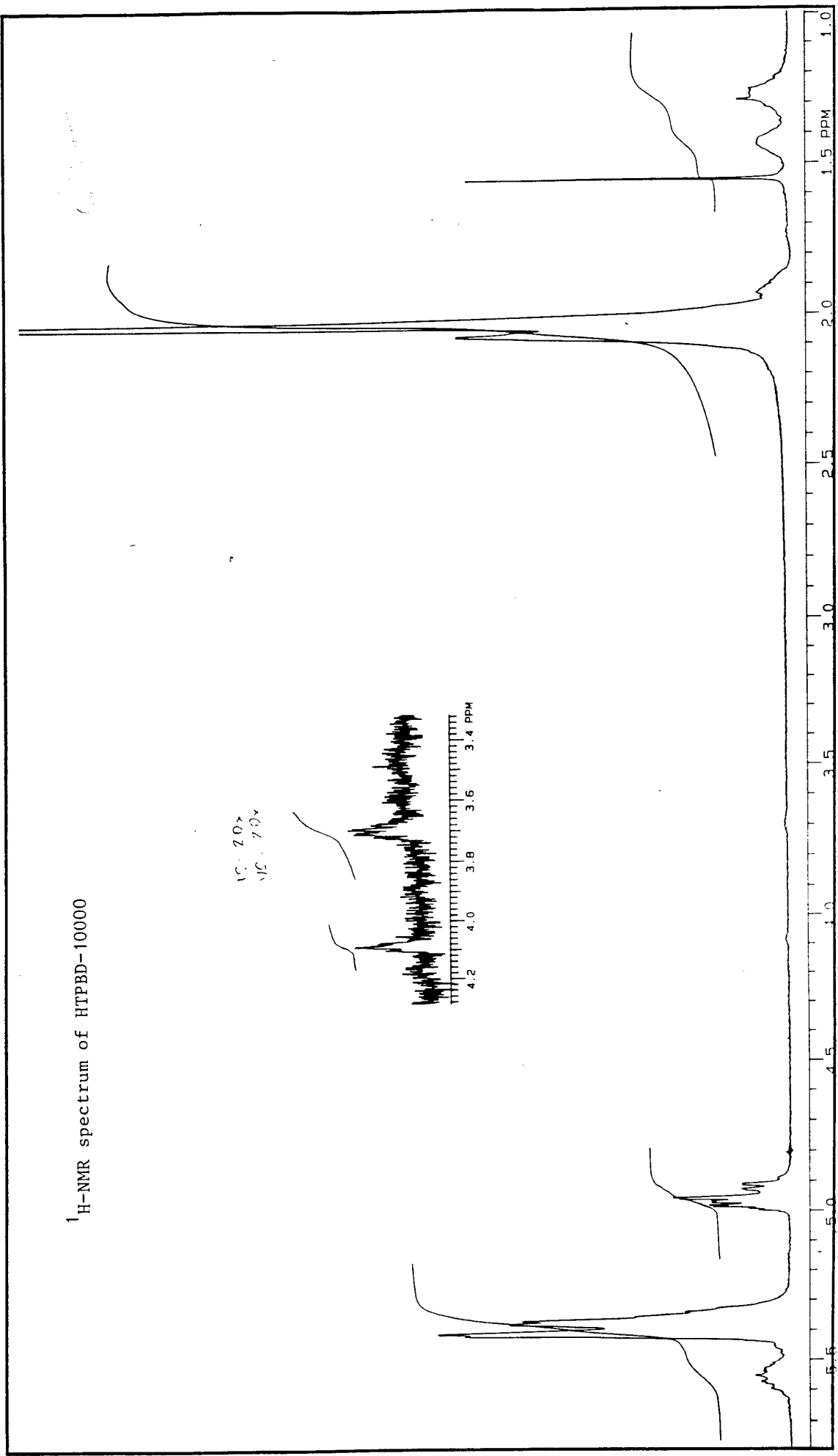
PLOT/PROCESSING

Nucleus \_\_\_\_\_ 15.0 Hz  
 Mode \_\_\_\_\_ 20.0 db  
 Modulation Mode \_\_\_\_\_ C  
 Pulse Width \_\_\_\_\_ msec  
 Power Mode \_\_\_\_\_

DECOUPLE

Nucleus \_\_\_\_\_ 400 MHz  
 Spec Width 5000.5 Hz  
 Acq Time 3.994 sec  
 Pulse Width 7.0 msec  
 Transients 16

058380



## **ANNEX 2**

### **CHARACTERIZATION OF HTPPE SAMPLES**

- ◆ Molecular weight distribution of precursor HTPBD-1000
- ◆ Molecular weight distribution of precursor HTPBD-1500
- ◆ Molecular weight distribution of precursor HTPBD-2000
- ◆ Molecular weight distribution of precursor HTPBD-3000
- ◆ Molecular weight distribution of precursor HTPBD-5000
- ◆ Molecular weight distribution of precursor HTPBD-10000
- ◆ FT-IR spectrum of precursor HTPBD-1000
- ◆ FT-IR spectrum of precursor HTPBD-1500
- ◆ FT-IR spectrum of precursor HTPBD-2000
- ◆ FT-IR spectrum of precursor HTPBD-3000
- ◆ FT-IR spectrum of precursor HTPBD-5000
- ◆ FT-IR spectrum of precursor HTPBD-10000
- ◆ Proton-NMR spectra of precursor HTPBD-1000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-1500 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-2000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-3000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-5000 and hydrogenated product
- ◆ Proton-NMR spectra of precursor HTPBD-10000 and hydrogenated product

VISCOLTEK CORP.

UCAL 4.05

ENDED: 10/01/96 12:12

FILENAME: 1741a

RUN ID: 96/182 Polibut. 174/1a

Mn = 1.21E3

Mw = 1.87E3

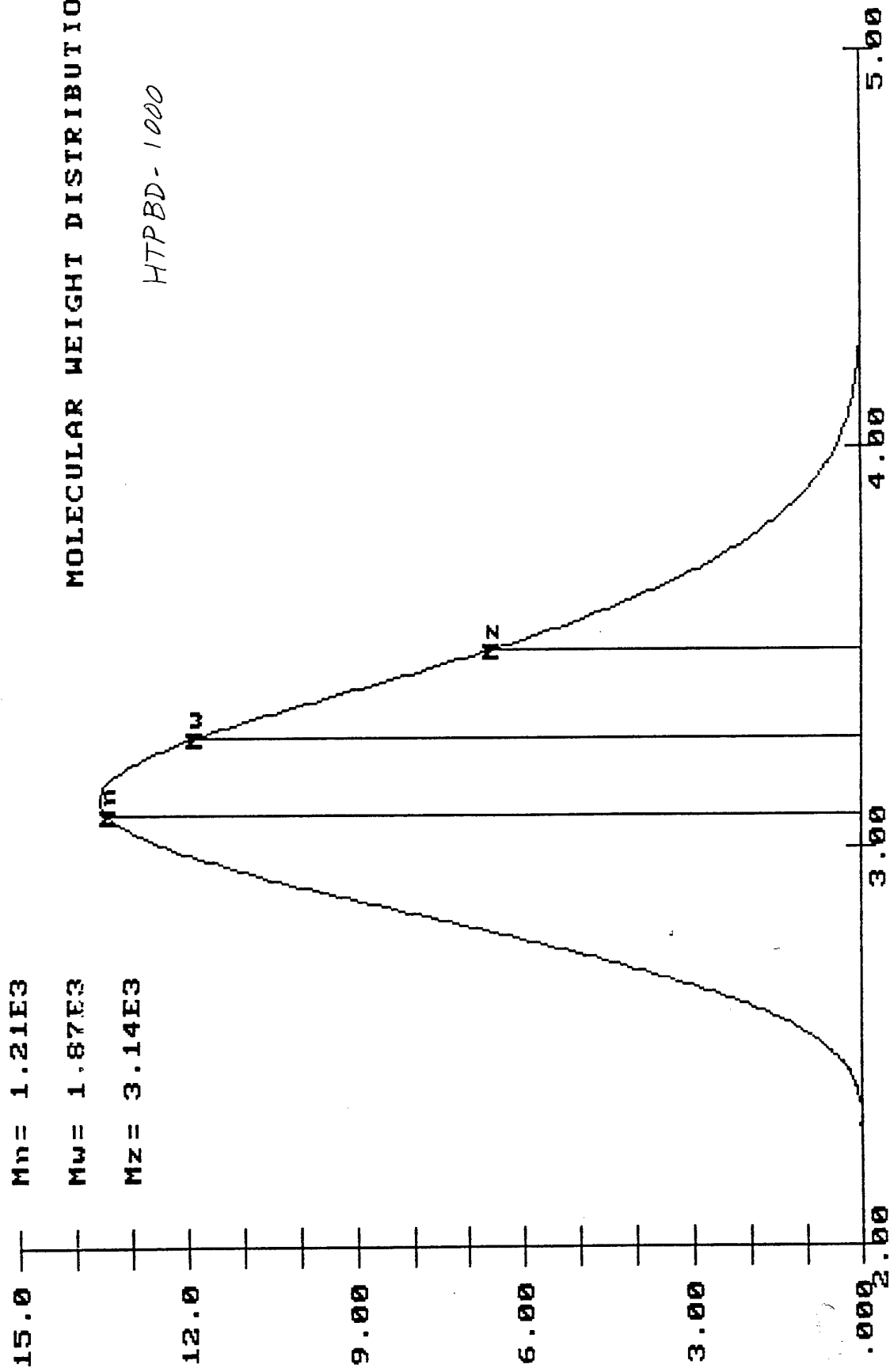
Mz = 3.14E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD-1000

1-01 x

(M501) uM

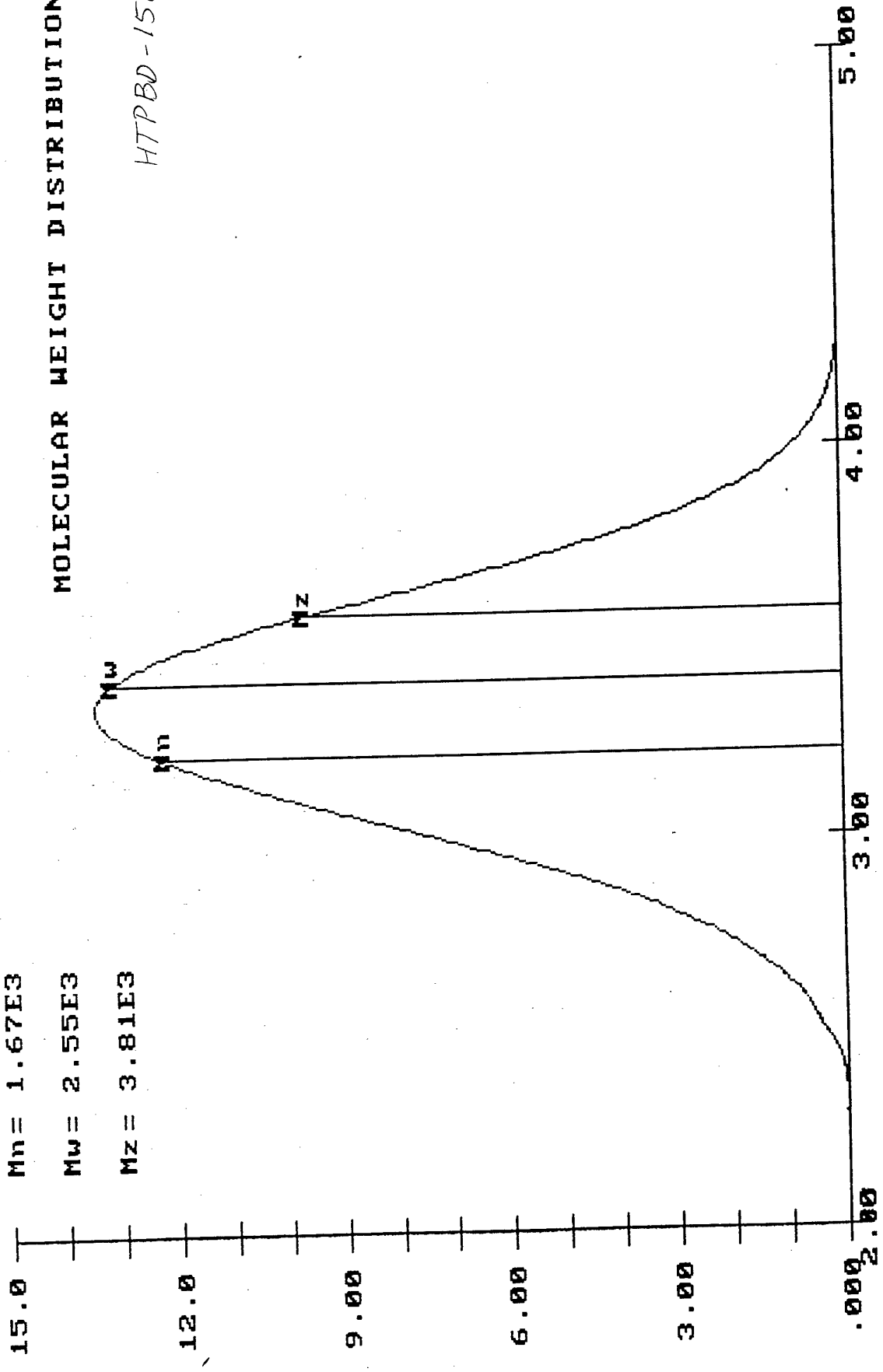


COTEK CORP. UCAL 4.05 ENDED: 10/01/96 13:26  
ENAME: 174k2 RUN ID: 96/184 Polibut. 174/k2

Mn = 1.67E3  
Mw = 2.55E3  
Mz = 3.81E3

MOLECULAR WEIGHT DISTRIBUTION

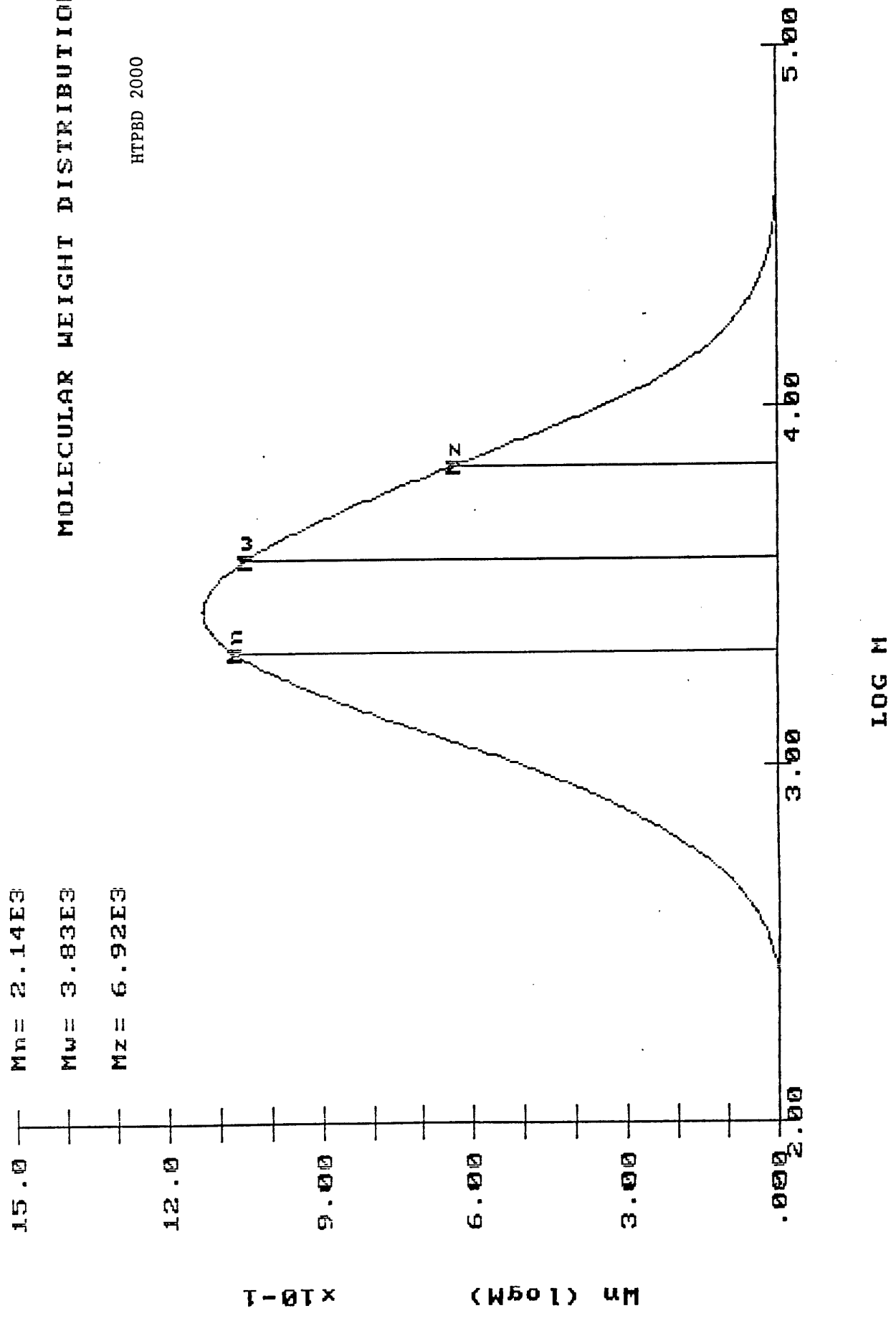
HTPBD-1500



VISCONTEN CORP.      UCAL 4.05      ENDED: 09/24/96    12:01  
 FILENAME: 161K      RUN ID: 96/175 Polibut. 161/K

MOLECULAR WEIGHT DISTRIBUTION

HTPBD 2000

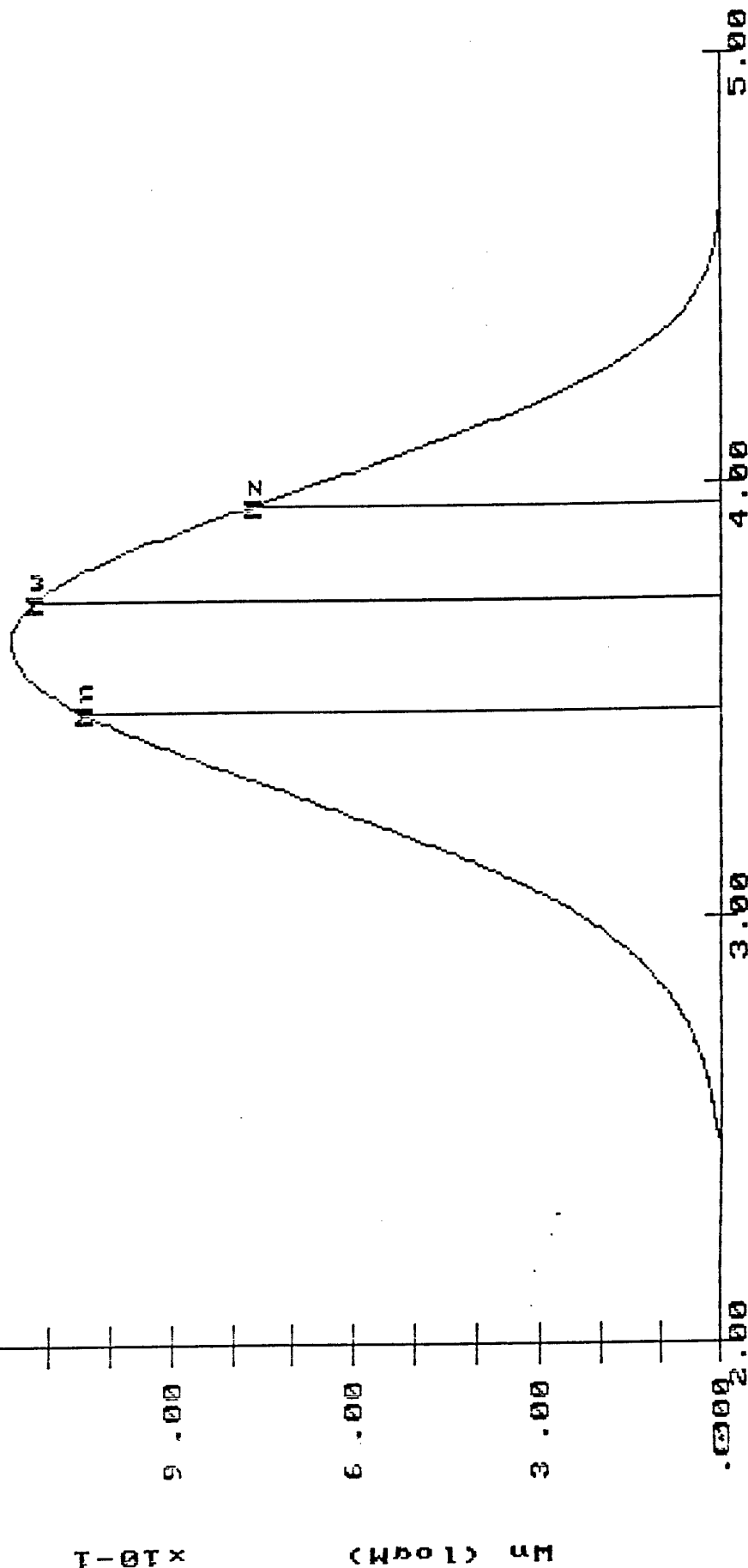


VISCONTEK CORP. UCAL 4.05 ENDED: 08/13/96 13:45  
 FILENAME: 154160 RUN ID: 96/143 Polibut. 154,160 mnta

Mn = 3.06E3  
 Mw = 5.44E3  
 Mz = 9.06E3

MOLECULAR WEIGHT DISTRIBUTION

HTPBD 3000



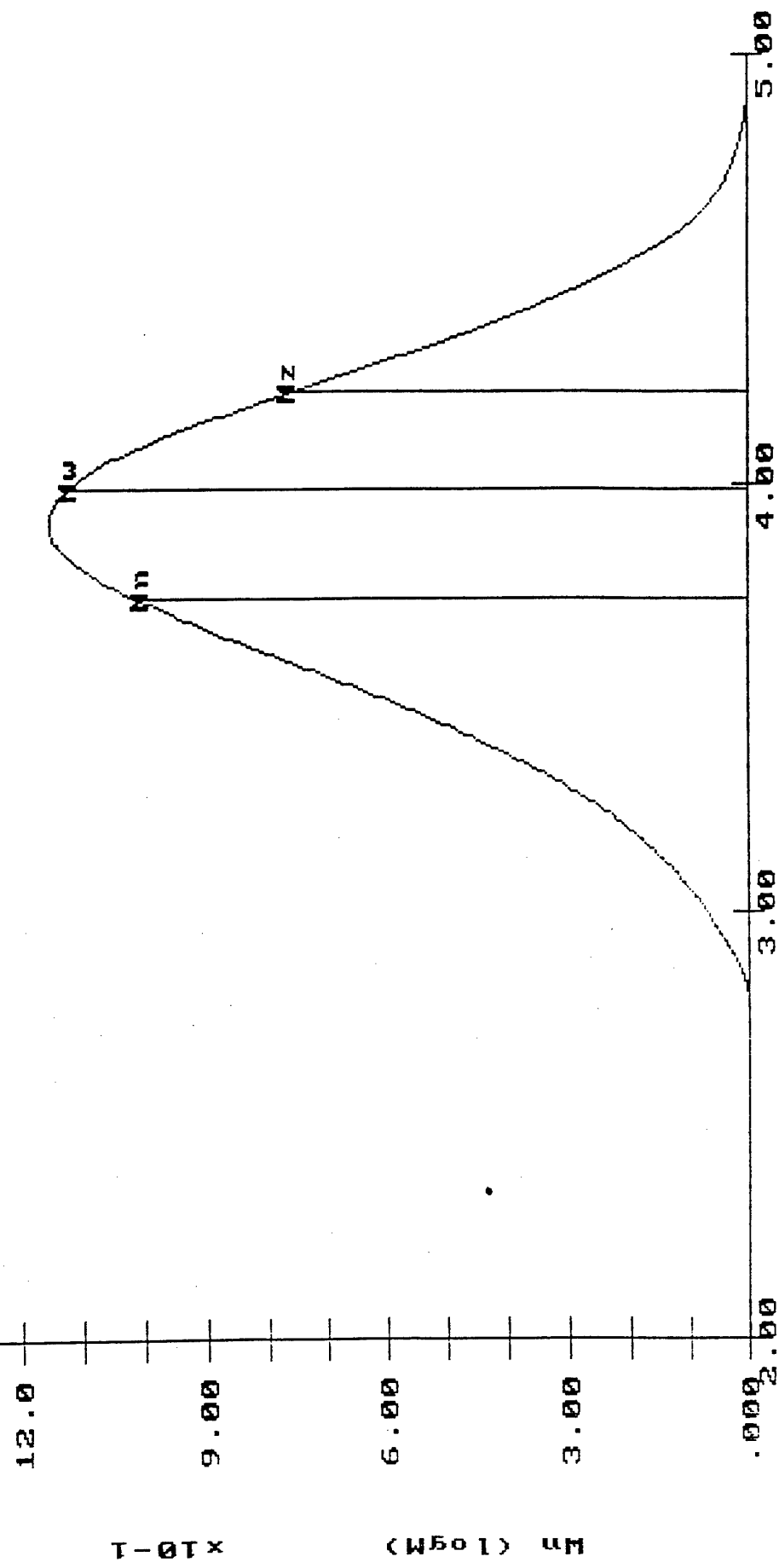
END M

FILENAME: 1751 RUN ID: 96/185 Polibut. 175/1

Mn= 5.40E3  
Mw= 9.76E3  
Mz= 1.63E4

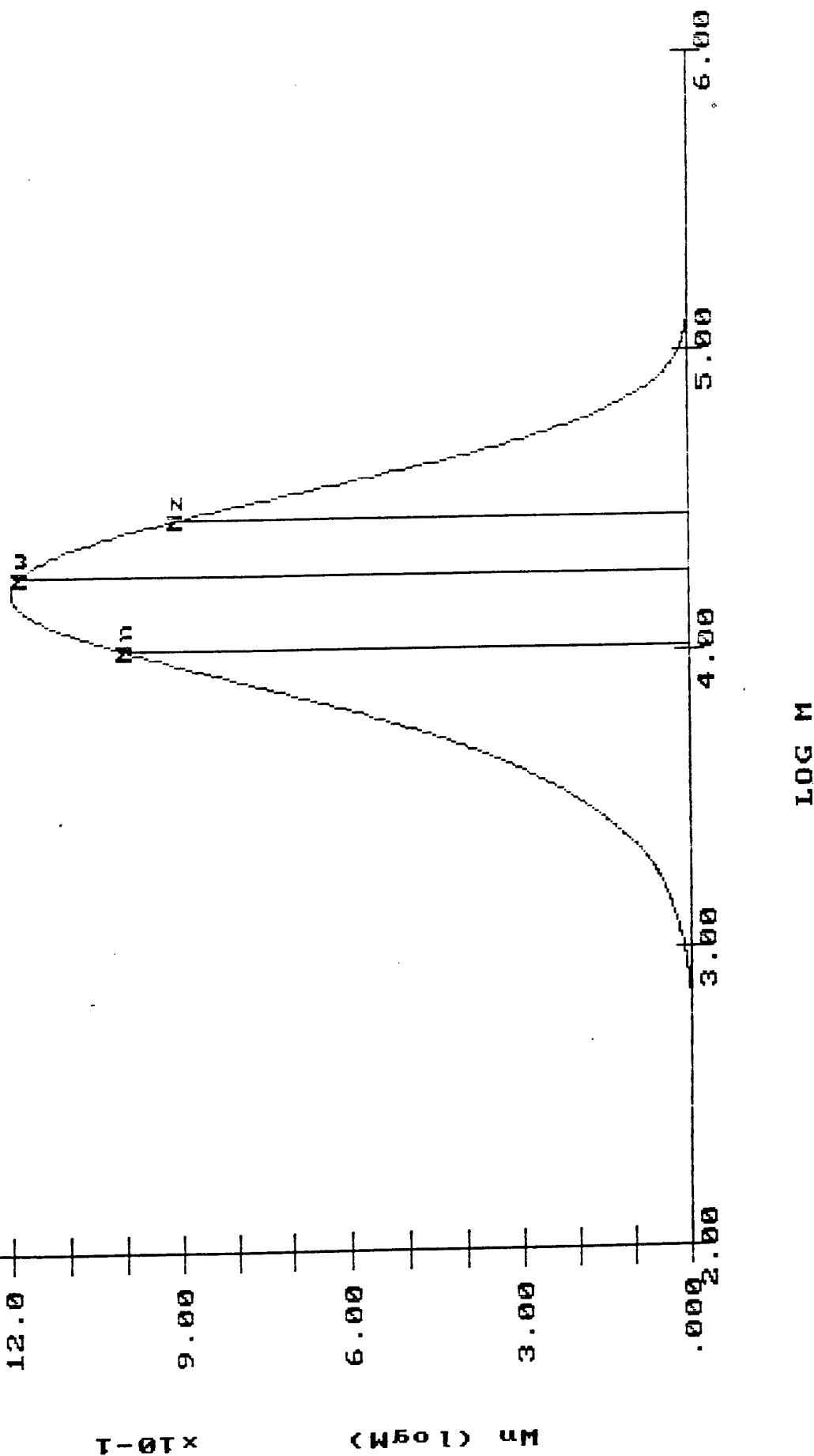
MOLECULAR WEIGHT DISTRIBUTION

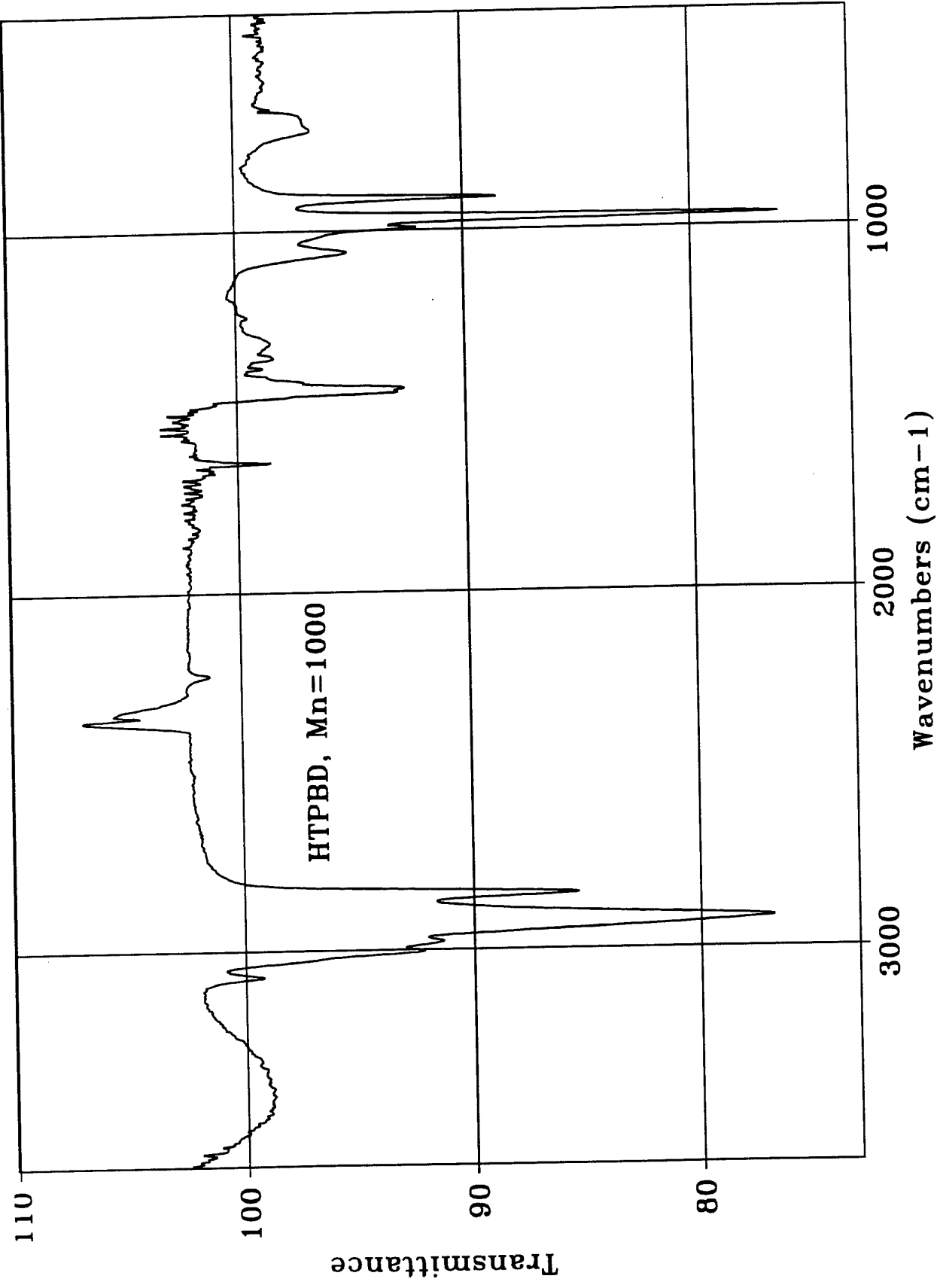
HTP BD-5000



LOG M

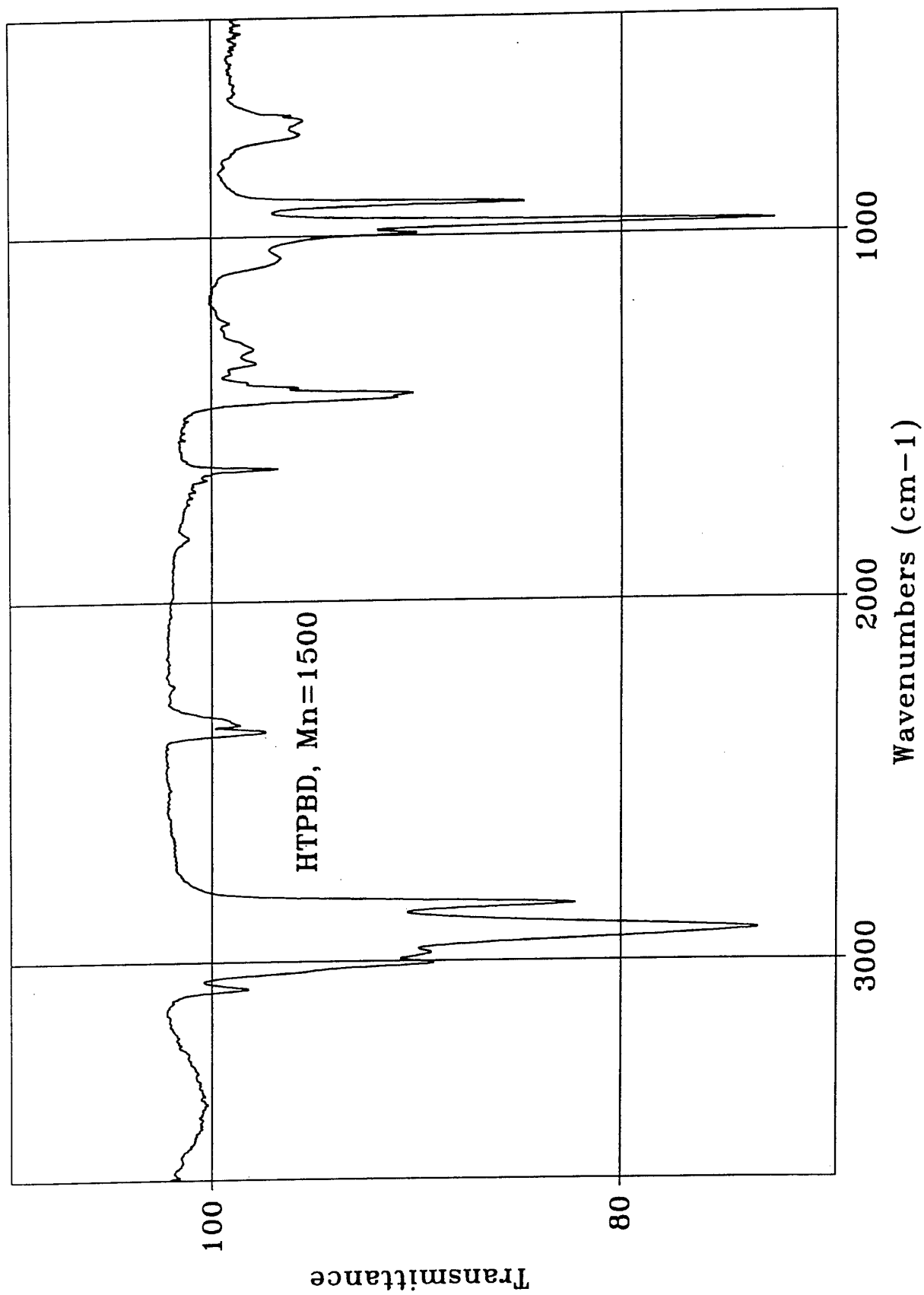
VISCOTEK CORP. UCAL 4.05 ENDED: 09/09/96 12:55  
 FILENAME: 167fob RUN ID: 96/158 Polibut. 167/fob  
 Mn = 1.03E4  
 Mw = 1.33E4  
 Mz = 2.86E4  
 MOLECULAR WEIGHT DISTRIBUTION  
 HTPBD - 10000





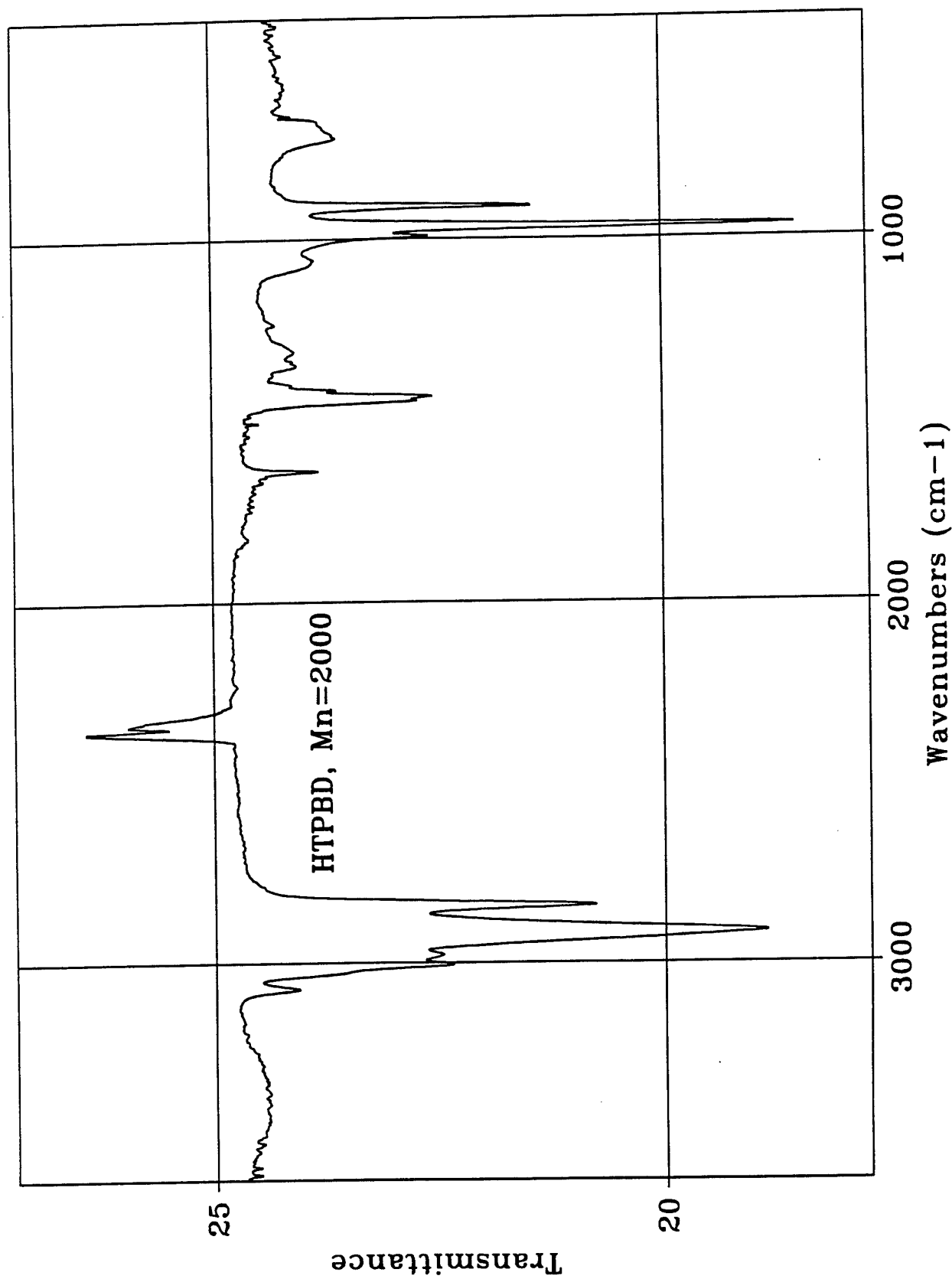
01/29/97 02:28

Res= 4 cm<sup>-1</sup>



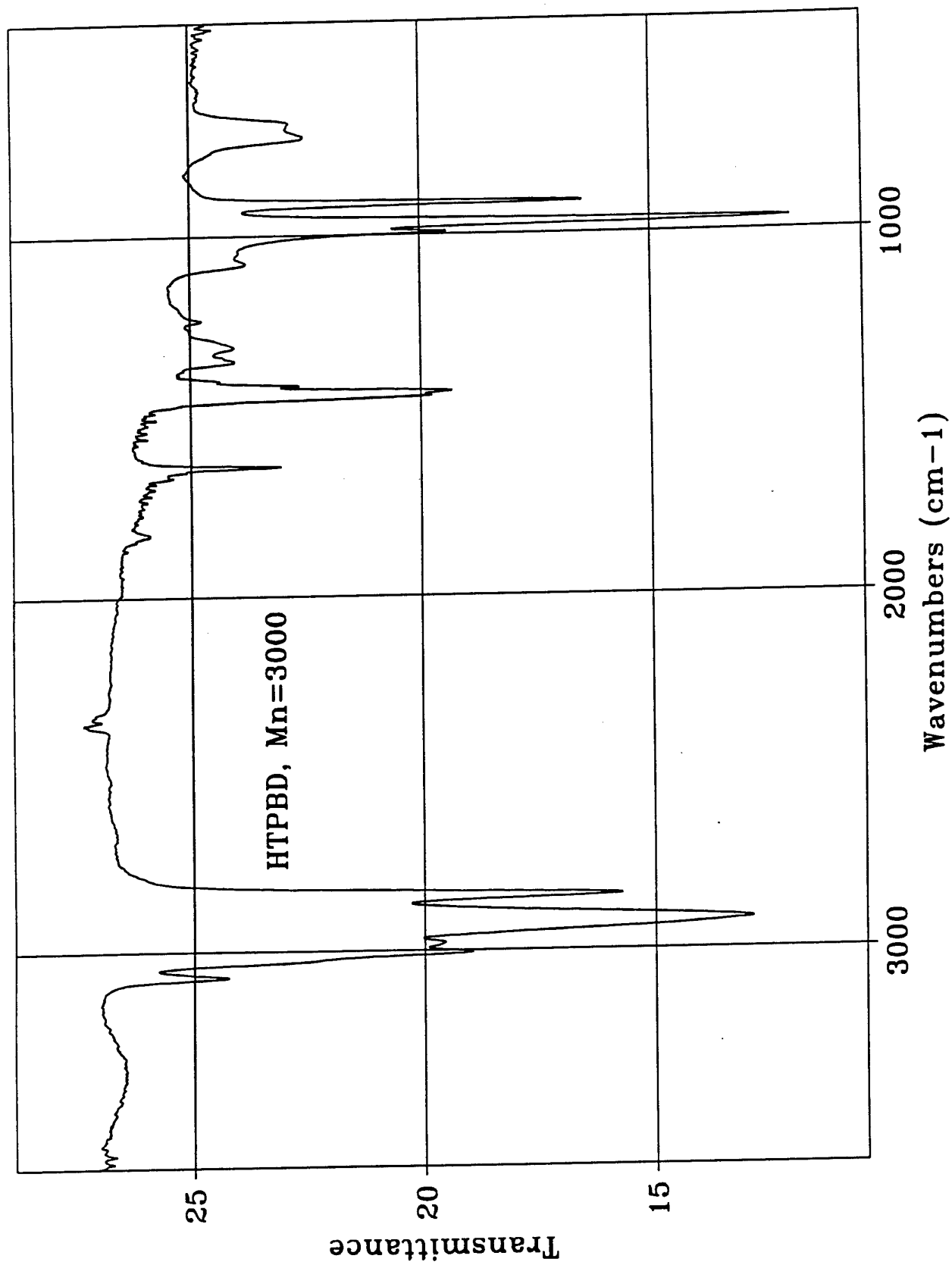
01/29/97 02:37

Res= 4 cm<sup>-1</sup>



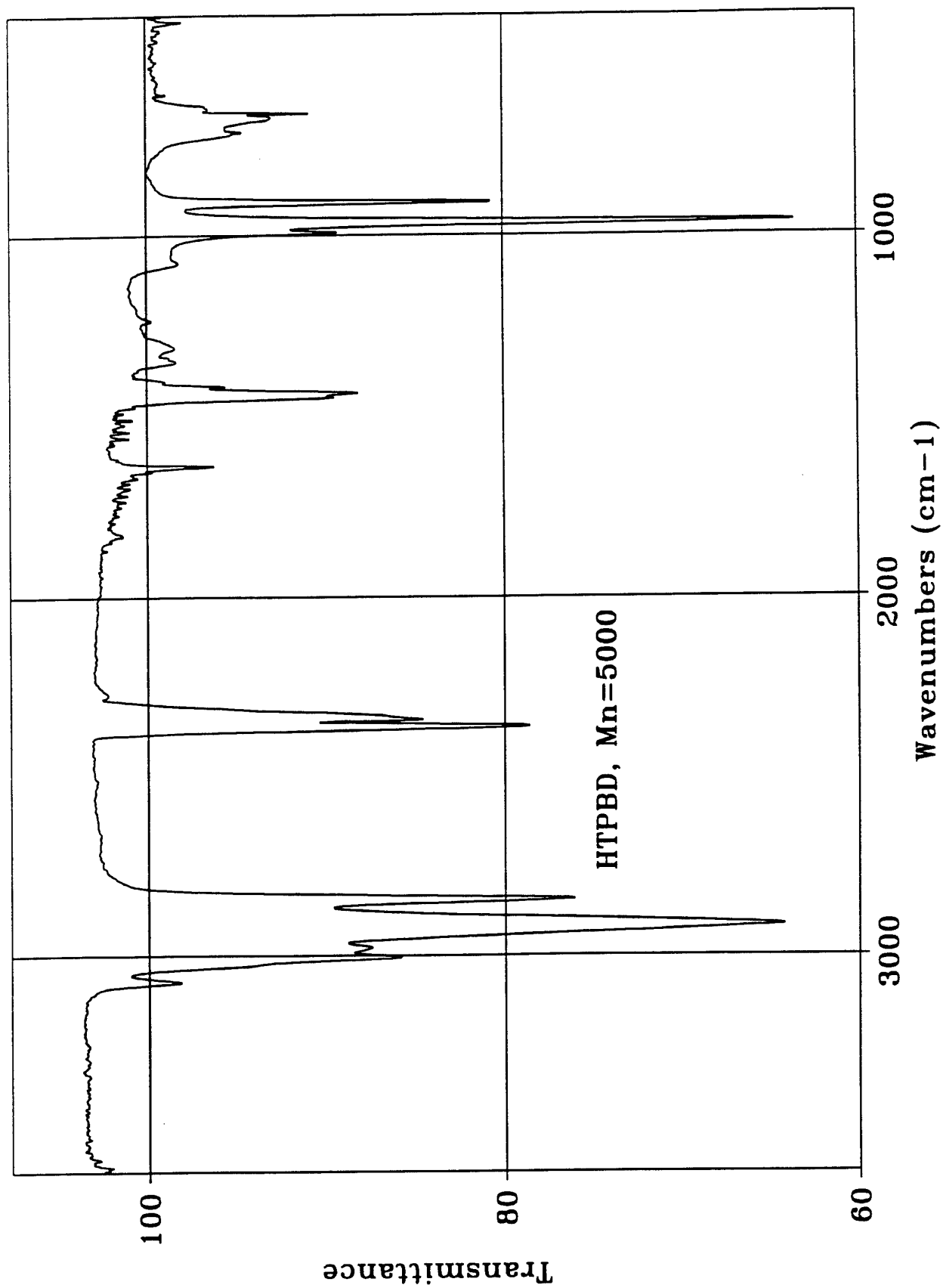
01/29/97 02:45

Res= 4 cm<sup>-1</sup>

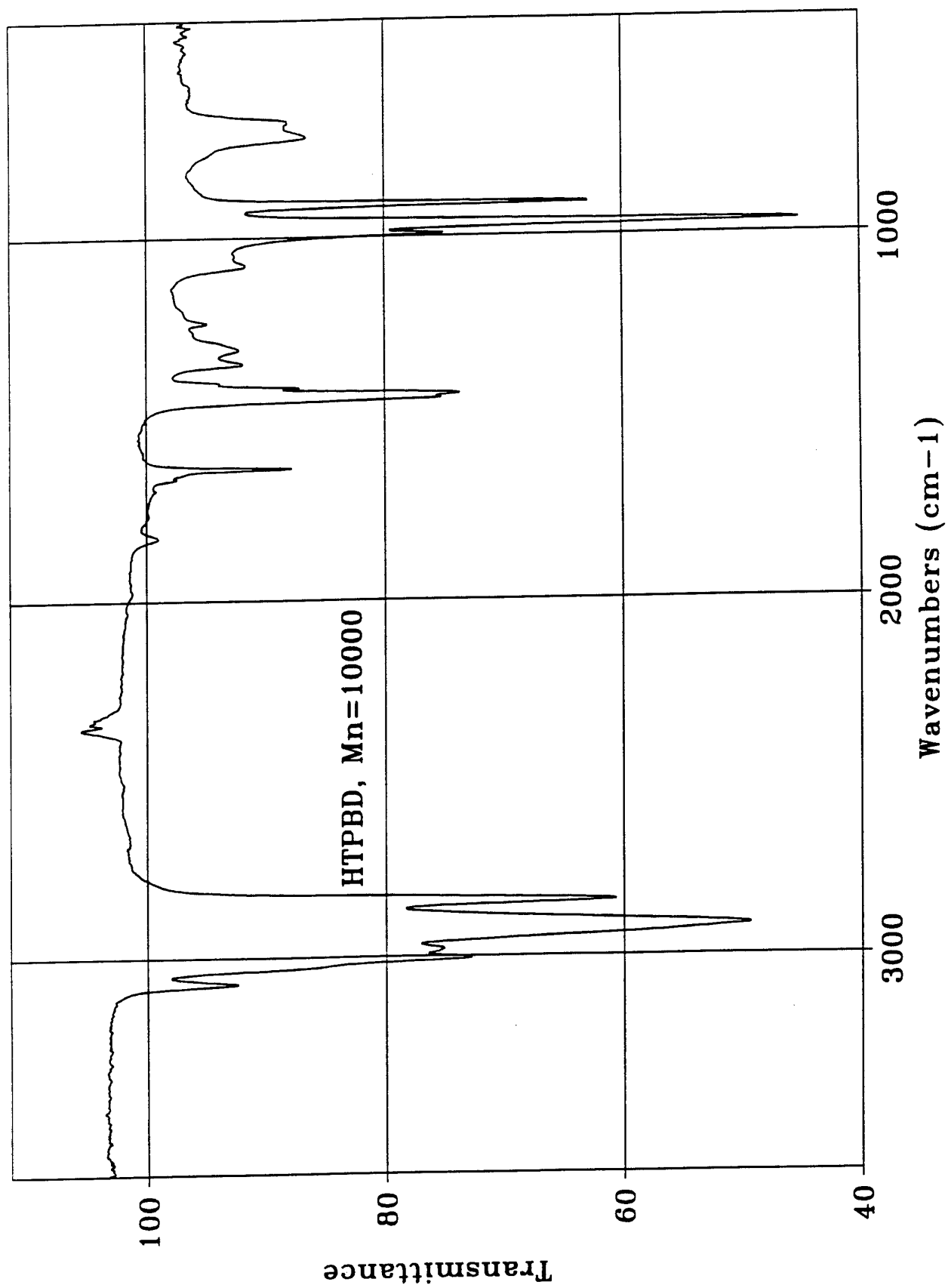


Res= 4 cm<sup>-1</sup>

01/29/97 02:52



Res= 4 cm-1



Res= 4 cm<sup>-1</sup>

HTPBD-1000

IS: 10 \*



Number \_\_\_\_\_  
File \_\_\_\_\_  
Date 08-10-96  
XL YXR 400varian

SAMPLE  
H-9920 (21023)  
HTPBD-1E3 (CDCL3)  
KELLER F./G.E.

Pulse Sequence: STD1H  
Tube OD: \_\_\_\_\_ mm  
Temp: \_\_\_\_\_ °C  
Solvent: CDCL3

EXPERIMENT  
P1: 32 K RE \_\_\_\_\_ sec  
L1: \_\_\_\_\_ Hz AF \_\_\_\_\_ sec  
Width: 2180.1 Hz/ppm Start 198.8 Hz/ppm  
Reference \_\_\_\_\_

OSCILLATOR  
Nucleus: 1.750  
Mode: NNN  
Modulation Mode: C  
Pulse Width: \_\_\_\_\_ µsec

RECEIVER  
Freq: 400 MHz  
Offset: -174.8 Hz  
Delay: 0 sec  
Transients: 16

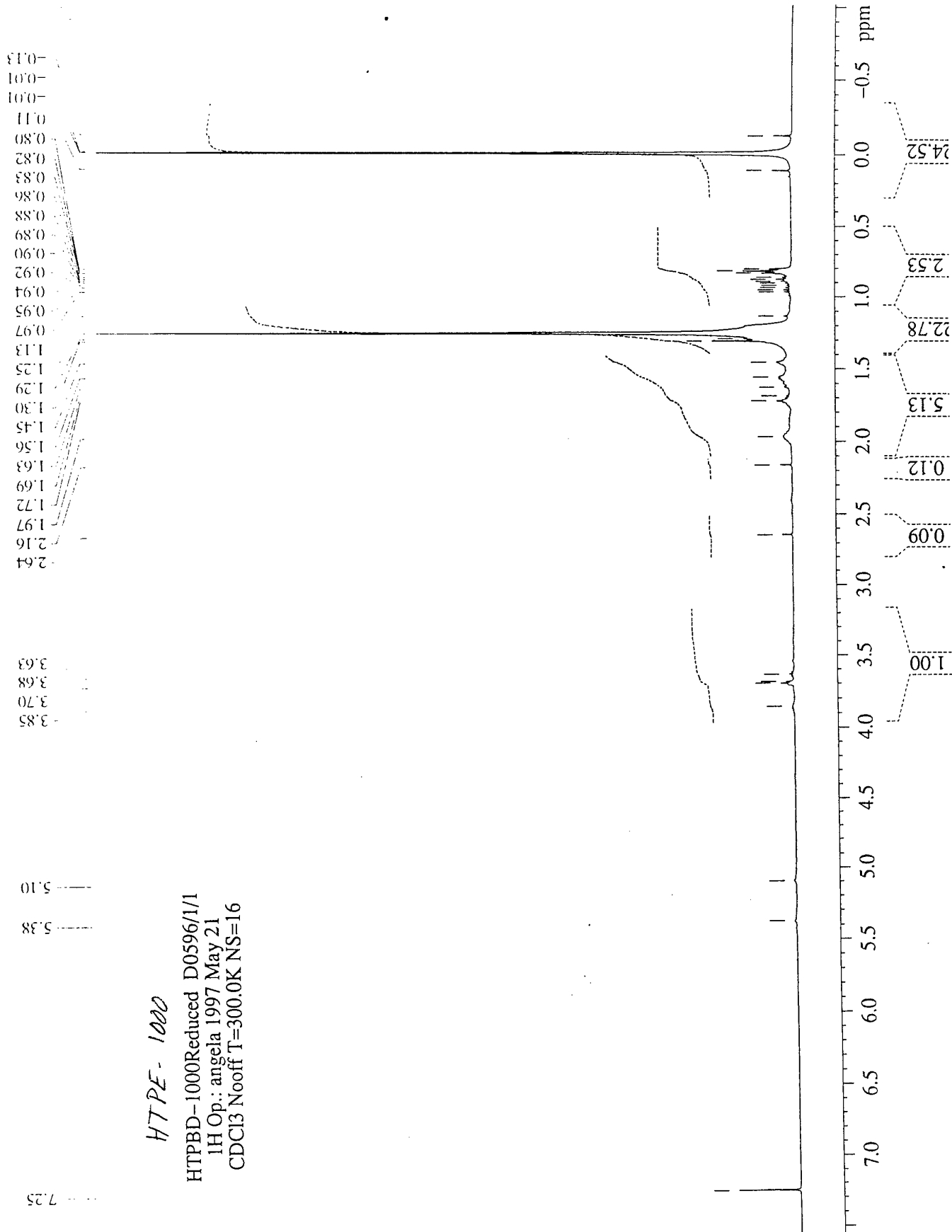
OSDSO  
Spec Width: 5988.8 Hz  
Acq Time: 3.995 sec  
Pulse Width: 7.0 µsec

HTPE-1000

HTPBD-1000Reduced D0596/1/1

1H Op.: angela 1997 May 21

CDC13 Nooff T=300.0K NS=16



045359VE

Nucleus 1 750 Freq 400 MHz  
Spec. Wdth 5008 B. Hz Offset -17.4 B. Hz  
Acq. Time 3.985 sec Delay 0 sec

DECOUPLE

Nucleus 1 750 Offset 75 0 Hz  
Mode NNN Power 20 dB  
Modulation: Mode C Freq 200 Hz

LOT/PROCESSING

PR 32 K RE --- sec CD --- sec  
LB --- Hz AF --- sec CD ---  
Wdth 2085 Hz/ppm Sst 321 Hz/ppm


EXPERIMENT

Pulse Sequence SID1H  
Tube OD --- mm  
Temp --- °C

SAMPLE

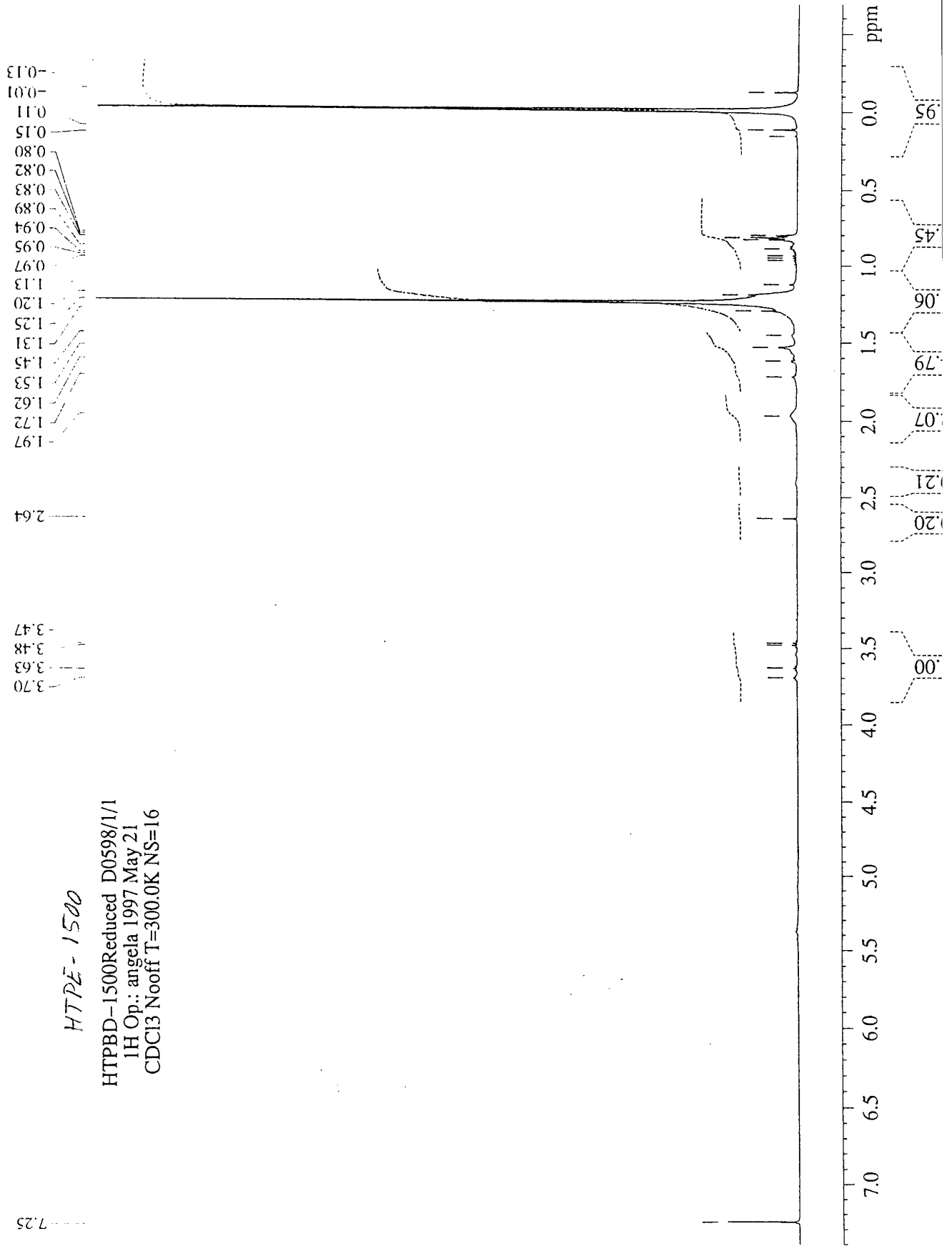
H-9947 (21023)  
HT80-SES (CDL3)  
KELLER F./6.E.

Number --- File --- H ---  
Date 08-10-95  
XL VXB ADDVATION



HTPE-1500

HTPBD-1500Reduced D0598/1/1  
1H Op.: angela 1997 May 21  
CDCl3 Nooff T=300.0K NS=16



HTPBD 2000

IS = 10 \*



Number \_\_\_\_\_  
 File \_\_\_\_\_  
 Date 08-10-95  
 XL VXR 400 variation

SAMPLE  
 H-9921 (21023)  
 HTPBD-2E3 (CDCL3)  
 KELLER F./G.E.

Pulse Sequence STD4H  
 Tube OD \_\_\_\_\_ mm  
 Temp \_\_\_\_\_ °C  
 Solvent CDCL3

EXPERIMENT

FN 32 K RE \_\_\_\_\_ sec  
 LB \_\_\_\_\_ Hz AF \_\_\_\_\_ sec  
 Width 2062.2 Hz/gpm Start 298.4 Hz/gpm  
 Reference \_\_\_\_\_

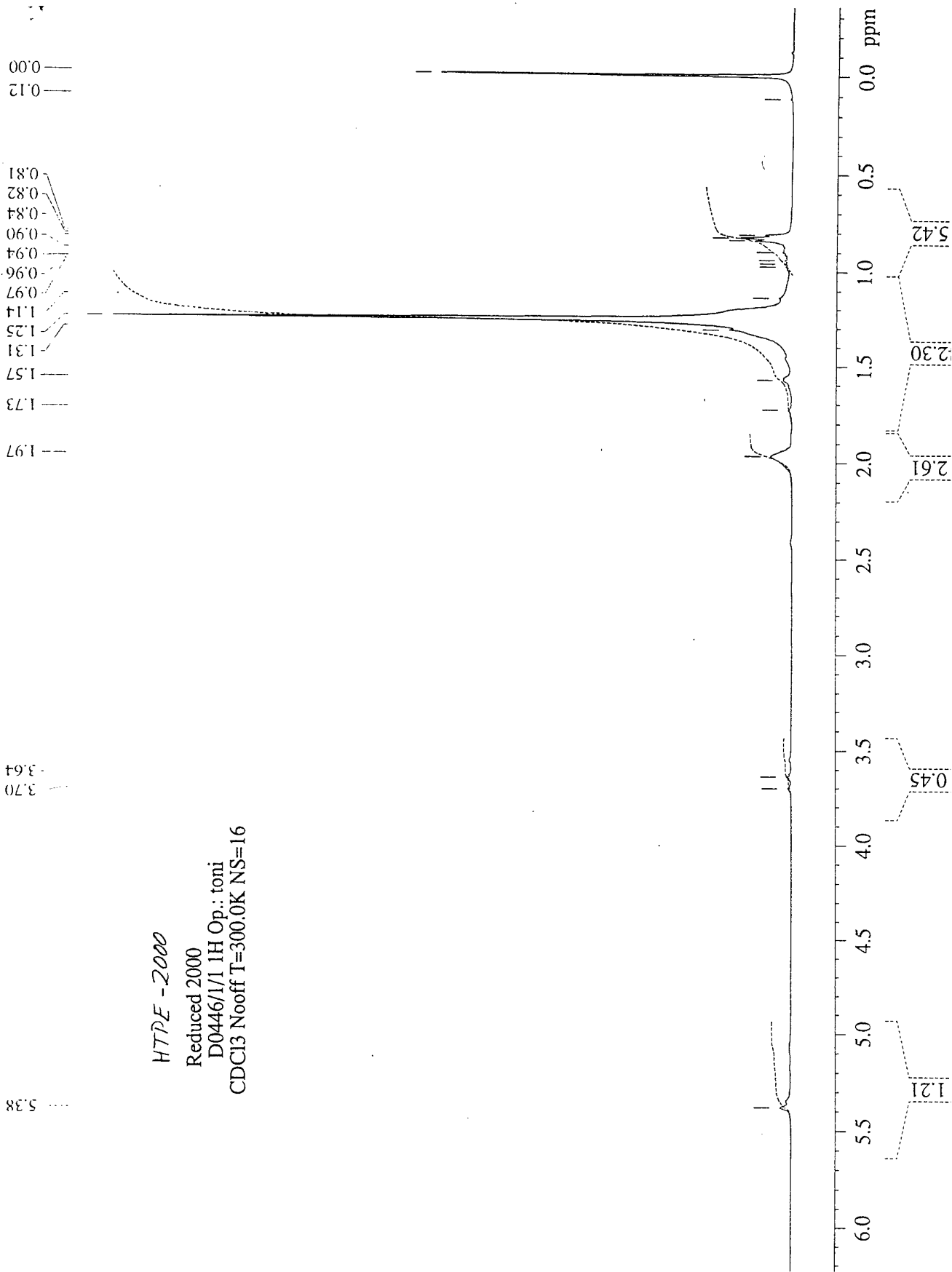
DECOMPT

Nucleus 1.750 Other 75.0 Hz  
 Mode NNN Power 20 db  
 Modulation Mode C Freq 200 Hz  
 Pulse Width \_\_\_\_\_ sec  
 Power Mode \_\_\_\_\_

RECEIPT

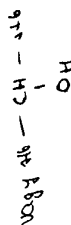
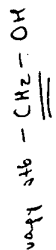
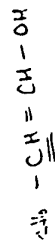
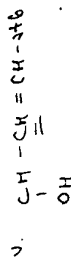
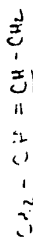
Nucleus 1.750 Freq 400 MHz  
 Spec Width 5998.8 Hz Other -174.8 Hz  
 Acq Time 3.995 sec Delay 0 sec  
 Pulse Width 7.0 sec Transmits 16

080300

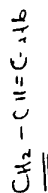
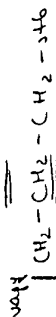
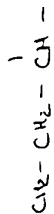
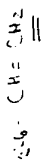


HTPE -2000  
Reduced 2000  
D0446/1/1 1H Op.: toni  
CDCl3 Nooff T=300.0K NS=16

HTPBD 3000



IS = 10 \*



3AM3588

Observed  
Nucleus:  $^1\text{H}$  Freq: 400 MHz  
Spec Width: 5998.8 Hz Offset: -174.8 Hz  
Acq Time: 3.995 sec Delay: 0 sec  
Pulse Width: 7.0  $\mu\text{sec}$  Transients: 16

Plot/Processing  
F1: 32 K RE sec CD: sec  
IR: Hz AF: sec CD: sec  
Width: 2126.7 Hz/gpm Start: 239.8 Hz/gpm  
Reference:  $\text{CDCl}_3$

Experiment  
Pulse Sequence: STD4H  
Tube OD: mm  
Temp:  $^{\circ}\text{C}$   
Solvent:  $\text{CDCl}_3$

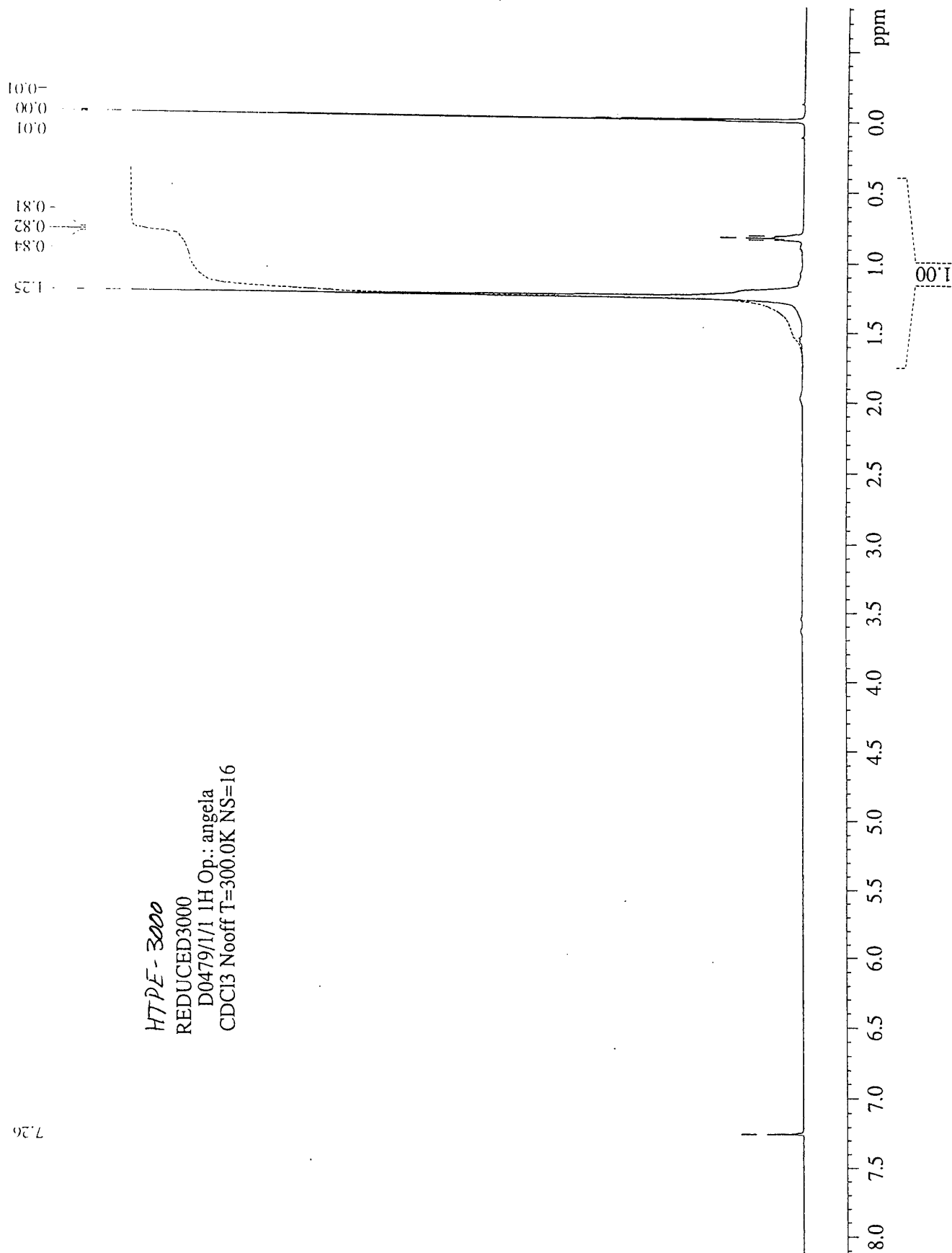
Sample  
H-9922 (21023)  
HTPBD-3E3 ( $\text{CDCl}_3$ )  
Keller / 6.E.

Number: KEE33  
File: KEE33  
Date: 08-10-95  
XL: VXR 400varian



7.26

H7PE-3000  
REDUCED3000  
D0479/1/1 1H Op.: angela  
CDCl3 Nooff T=300.0K NS=16



HTPDB-5000

IS: 10 \*



Number \_\_\_\_\_  
File \_\_\_\_\_ H  
Date 08-10-96  
XL VXR 400 varian

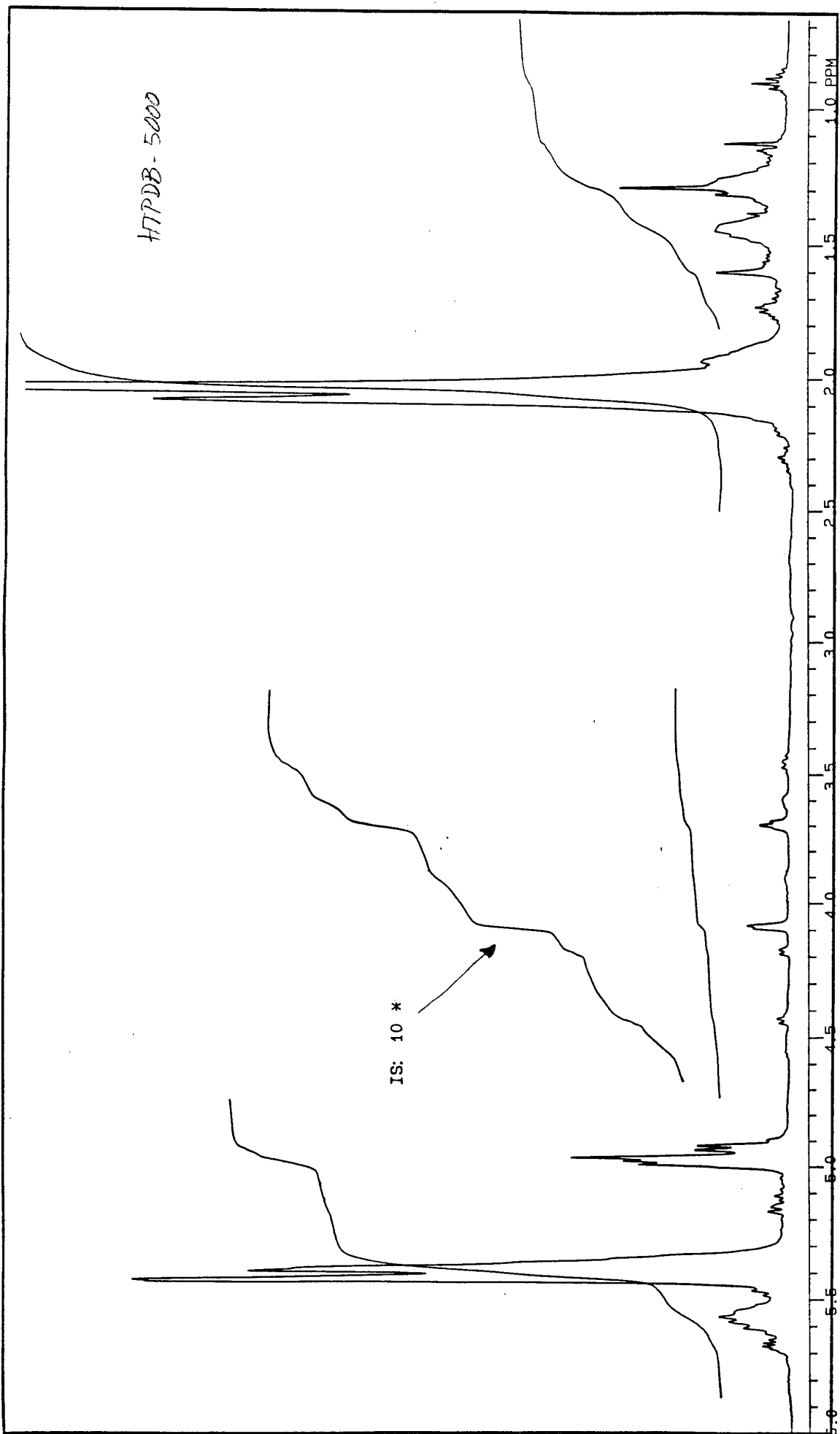
SAMPLE  
H-9919 (21023)  
HTPBD-1.5E3 (CDCL3)  
KELLER F./G.E.

Pulse Sequence STDH  
Tube OD \_\_\_\_\_ mm  
Temp \_\_\_\_\_ °C  
Solvent CDCL3

EXPERIMENT  
P1 \_\_\_\_\_ 32-K RE \_\_\_\_\_ sec CD \_\_\_\_\_ sec  
L1 \_\_\_\_\_ Hz AF \_\_\_\_\_ sec CD \_\_\_\_\_  
Width 2132.5 Hz/gm Scan 269.9 Hz/gm  
Reference \_\_\_\_\_

DECOUPLE  
Nucleus 13C-130 He  
Mode 30 dB  
Modulation Mode C  
Pulse Width 1.0 sec

OBSERVE  
Nucleus 13C-130 He  
Spec Width 9998.8 Hz  
Acq Time 3.995 sec  
Pulse Width 7.0 μsec

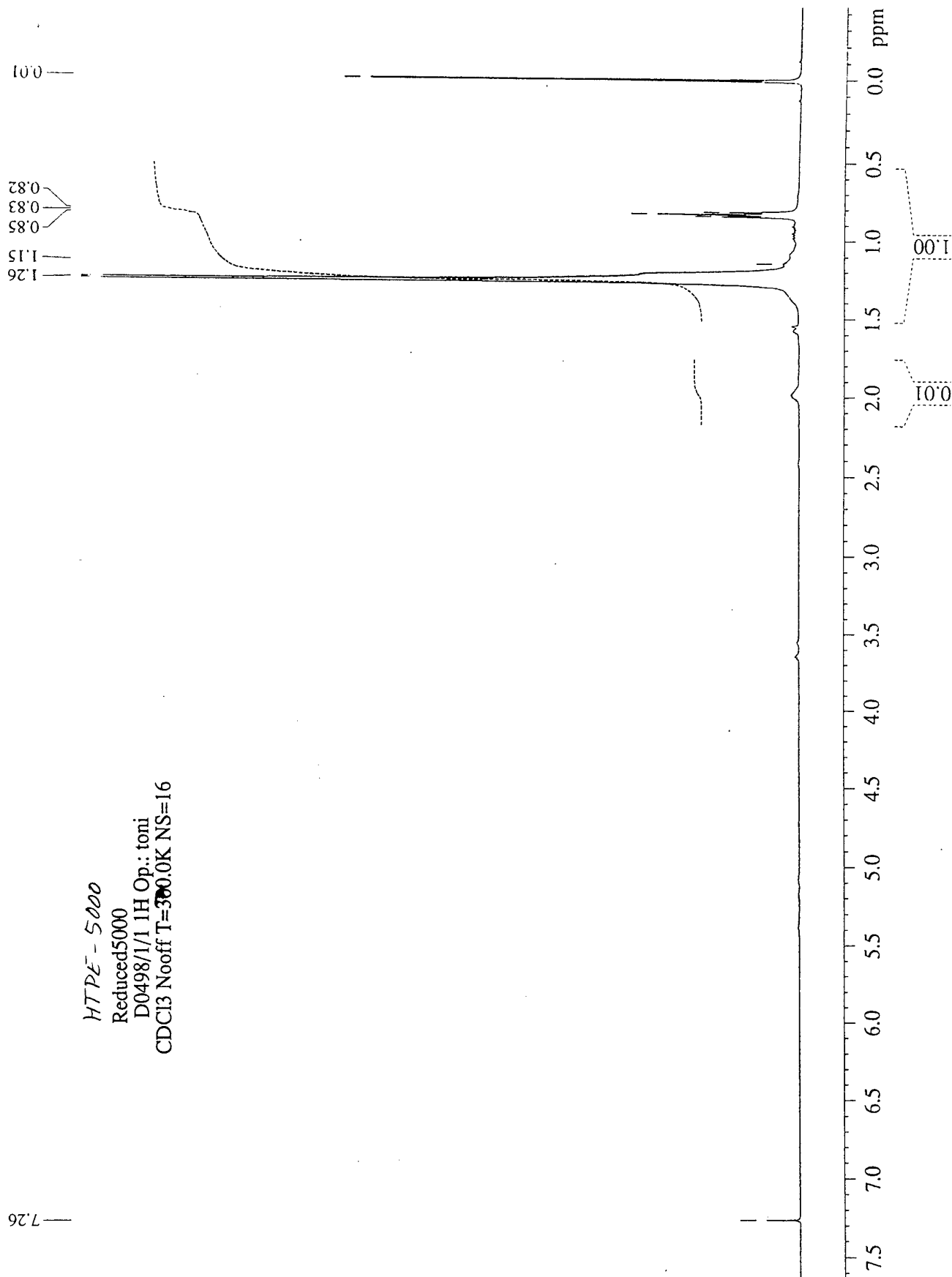


HTPE-5000  
Reduced5000  
D0498/1/1 1H Op.: toni  
CDC13 Nooff T=300.0K NS=16

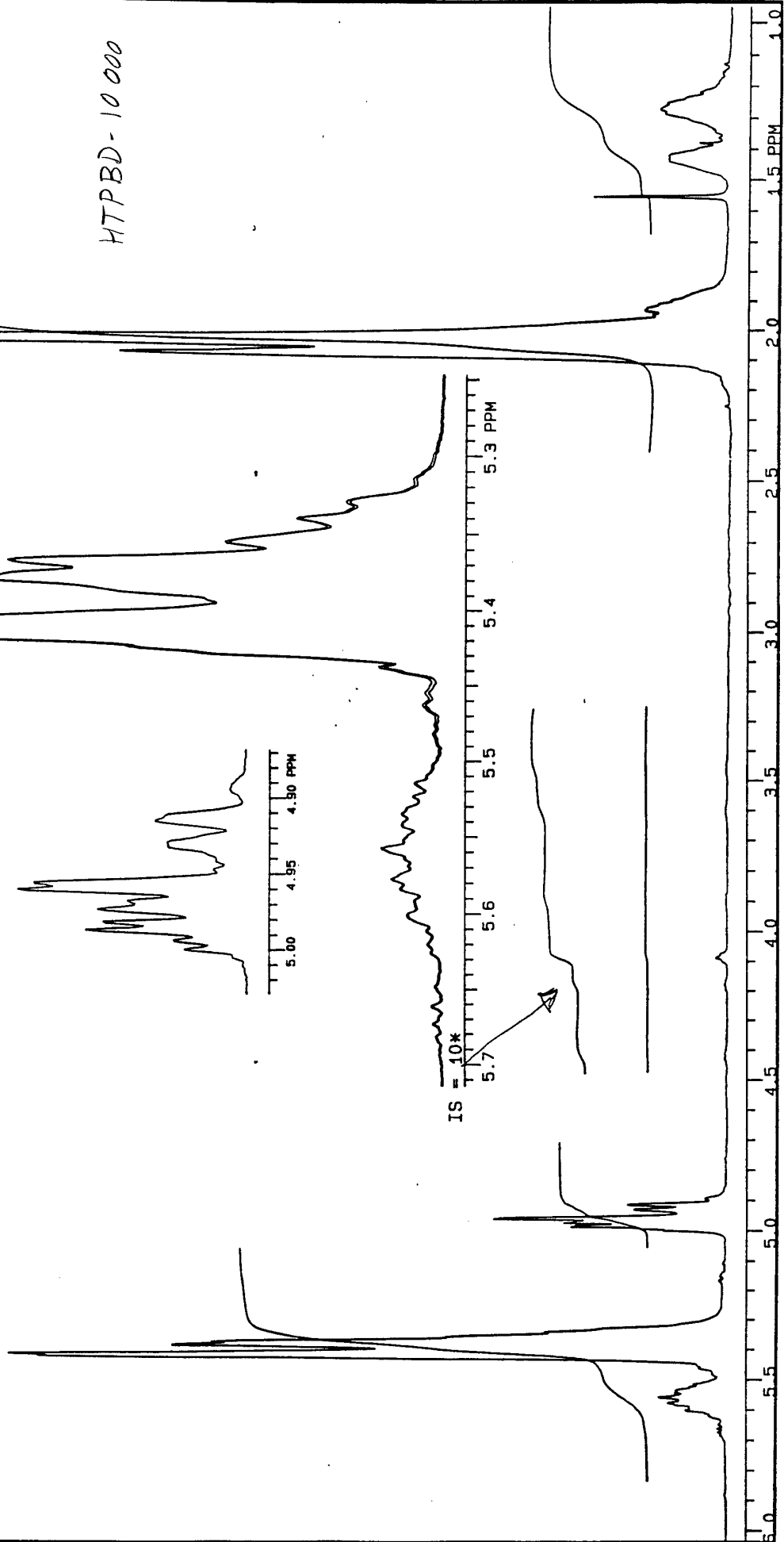
7.26

0.01

1.26  
1.15  
0.85  
0.83  
0.82



HTPBD-10 000



OBSERVE		PLOT/PROCESSING		EXPERIMENT		SAMPLE		Number	
Nucleus	1.750	Offset	75.0	Hz	FN	32	K	RE	---
Spec. Width	5998.8	Hz	Mode	NNN	LB	---	Hz	AF	---
Acq. Time	3.995	sec	Modulation	Mode	Width	2034.0	Hz/ppm	Start	380.1
Pulse Width	7.0	sec	Pulse Width	---	Reference	---	---	---	---
Decouple	---	---	Decouple	---	Reference	---	---	---	---
Transients	15	---	Transients	---	Reference	---	---	---	---
Delay	0	sec	Delay	---	Reference	---	---	---	---
Offset	-174.8	Hz	Offset	---	Reference	---	---	---	---
Power	20	db	Power	---	Reference	---	---	---	---
Tube O.D.	---	mm	Tube O.D.	---	Reference	---	---	---	---
Temp	---	°C	Temp	---	Reference	---	---	---	---
Solvent	CDCL3	---	Solvent	---	Reference	---	---	---	---
Sample	H-9918 (21023)	---	Sample	---	Reference	---	---	---	---
HTPBD-1E4 (CDCL3)	---	---	HTPBD-1E4 (CDCL3)	---	Reference	---	---	---	---
KELLER F./S.E.	---	---	KELLER F./S.E.	---	Reference	---	---	---	---
Date	08-10-96	---	Date	---	Reference	---	---	---	---
File	H	---	File	---	Reference	---	---	---	---
XL	VXR	400varian	XL	---	Reference	---	---	---	---

7.26

HTPE- 10.000  
Reduced 10000  
D0496/1/1 1H Op.: toni  
CDCl3 Nooff T=300.0K NS=32

